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LXI.—ON SUBSTITUTED PYROMUCIC ACIDS.

SECOND PAPER.

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(Continued from p. 391.)

β-SULPHO-δ-BROMPYROMUCIC ACID.

The three sulphonic acids thus far described contain the sulpho-group in the δ position, and, in the two cases where the formation of isomeric products is theoretically possible, we have hitherto been unable to prove that any isomeric sulphonic acids are in reality formed. For the preparation of such isomeric products it was, therefore, evidently necessary to start with the δ-hydrogen atom otherwise replaced, and the δ-brompyromucic acid formed the most convenient material. We found no difficulty in preparing in this way a sulphonic acid which we have called the β-sulpho-δ-brompyromucic acid and from it the β-sulphopyromucic acid itself may be made. Since the brominated acid was of necessity first prepared, and we were able to investigate it more fully, it may be more conveniently first described.

δ-Brompyromucic acid dissolves in fuming sulphuric acid without essential decomposition, and after the lapse of some time the formation of the sulphonic acid appears to be complete. On neutralising the diluted solution with baric carbonate, a barium

salt is obtained which is sparingly soluble even in hot water, and which usually persistently retains a slight yellow or greenish color. The purification of this neutral salt is still further rendered difficult by the fact that a hot saturated solution of the salt deposits little or nothing on cooling, and recrystallisation therefore involves the evaporation of comparatively large quantities of liquid. The purification may be more conveniently effected by conversion into the more soluble acid salt, or by preparing the acid salt at the outset. The acid salt may easily be made by dissolving the neutral salt in hydrochloric acid somewhat diluted with water, and removing by recrystallisation the baric chloride formed. From a solution of the acid salt the neutral salt may again be precipitated by the addition of baric acetate, or of course by the addition of ammonic hydrate and the necessary quantity of baric chloride. The free acid made from the barium salt by exact precipitation with sulphuric acid forms oblique flat prisms or plates which deliquesce in moist air.

Baric β-Sulpho-δ-brompyromucate, $BaC_5HBrSO_6 . 5H_2O$.—The barium salt is sparingly soluble in hot or cold water, and crystallises in clear six-sided, clustered prisms. Its aqueous solution is precipitated by the addition of alcohol. The salt contains five molecules of water, four of which it loses slowly on exposure to the air, or more rapidly when heated to 100°.

I. 2.1588 grams of the salt dried by short exposure to the air lost, at 162°, 0.3806 gram H_2O.

II. 1.1795 gram of the salt dried by short exposure to the air lost, at 170°, 0.2010 gram H_2O.

	Calculated for $BaC_5HBrSO_6.5H_2O$.	Found. I.	II.
H_2O	18.14	17.63	17.88

I. 1.8574 gram of the salt dried at 100° lost, at 162°, 0.0792 gram H_2O.

II. 0.7262 gram of the salt dried at 100° lost, at 160°, 0.0317 gram H_2O.

	Calculated for $BaC_5HBrSO_6.H_2O$.	Found. I.	II.
H_2O	4.25	4.28	4.37

I. 0.6945 gram of the salt dried at 160° gave 0.3980 gram $BaSO_4$.

II. 0.7840 gram of the salt dried at 140° gave 0.4500 gram $BaSO_4$.

III. 0.7825 gram of the salt dried at 140° gave 0.4495 gram $BaSO_4$.

	Calculated for BaC_5HBrSO_6.	Found. I.	II.	III.
Ba	33.75	33.69	33.75	33.77

We also determined the solubility of the salt in water at ordinary temperatures. Since the hot saturated solution deposited little or nothing on cooling, we prepared the solution by boiling down the hot aqueous solution until the salt began to separate. On cooling this supersaturated solution, abundant crystals were deposited.

I. 32.6032 grams of the solution saturated at 20° gave 0.5016 gram $BaSO_4$.

II. 33.7864 grams of the solution saturated at 20° gave 0.5194 gram $BaSO_4$.

The aqueous solution saturated at 20°, therefore, contained the following percentages of the anhydrous salt:

I.	II.
2.68	2.68

Acid Baric β-Sulpho-δ-brompyromucate, $Ba(C_5H_2BrSO_6)_2 4H_2O$.—This salt is most easily prepared by dissolving the neutral barium salt in diluted hydrochloric acid. It is readily soluble in hot water, sparingly in cold water, and crystallises in large well formed prisms which appear to be triclinic. The salt loses nothing when exposed to the air, or over sulphuric acid, and the loss at 100° is also insignificant. At 130° it slowly loses in weight, but turns brown and suffers partial decomposition before complete dehydration is reached.

I. 0.7884 gram of the air-dried salt gave 0.2456 gram $BaSO_4$.

II. 0.7804 gram of the air-dried salt gave 0.2460 gram $BaSO_4$.

	Calculated for $Ba(C_5H_2BrSO_6)_2 \cdot 4H_2O$.	Found. I.	II.
Ba	18.29	18.32	18.53

Calcic β-Sulpho-δ-brompyromucate, $CaC_5HBrSO_6.2H_2O$.—The calcium salt is quite readily soluble in cold water, and its solubility is but little increased by heat. It crystallises in compactly aggregated oblique prisms, which are permanent in the air, and lose but little in weight over sulphuric acid or when heated to 100°.

I. 1.7804 gram of the air-dried salt lost, at 205°, 0.1767 gram H_2O.

II. 0.6483 gram of the air-dried salt gave 0.2544 gram $CaSO_4$.

	Calculated for $CaC_5HBrSO_6.2H_2O$.	Found. I.	II.
H_2O	10.42	9.92	
Ca	11.60		11.54

I. 0.4645 gram of the salt dried at 200° gave 0.2015 gram $CaSO_4$.

II. 0.4026 gram of the salt dried at 200° gave 0.1758 gram $CaSO_4$.

	Calculated for CaC_5HBrSO_6.	Found. I.	II.
Ca	12.94	12.76	12.83

Plumbic β-Sulpho-δ-brompyromucate, $PbC_5HBrSO_6.1\frac{1}{2}H_2O$.—The lead salt is tolerably soluble in cold water, and its solubility is but little increased by heat. The salt dried by exposure to the air contains one and a half molecules of water, one molecule of which it retains when dried over sulphuric acid.

I. 1.5047 gram of the air-dried salt lost, at 150°, 0.0815 gram H_2O, and gave 0.9074 gram $PbSO_4$.

II. 1.7254 gram of the air-dried salt lost, at 150°, 0.0925 gram H_2O.

III. 0.5361 gram of the air-dried salt gave 0.3239 gram $PbSO_4$.

	Calculated for $PbC_5HBrSO_6.1\frac{1}{2}H_2O$.	Found. I.	II.	III.
H_2O	5.37	5.42	5.36	
Pb	41.15	41.20		41.27

1.6958 gram of the salt dried over sulphuric acid lost, at 150°, 0.0629 gram H_2O.

	Calculated for $PbC_5HBrSO_6.H_2O$.	Found.
H_2O	3.64	3.71

I. 0.5894 gram of the salt dried at 150° gave 0.3743 gram $PbSO_4$.

II. 0.6496 gram of the salt dried at 150° gave 0.4122 gram $PbSO_4$.

	Calculated for PbC_5HBrSO_6.	Found. I.	II.
Pb	43.49	43.38	43.35

Argentic β-Sulpho-δ-brompyromucate, $Ag_2C_5HBrSO_6.2H_2O$.—The silver salt is sparingly soluble in cold water, and crystallises in plates which contain two molecules of water.

1.3888 gram of the air-dried salt lost, at 115°, 0.0968 gram H_2O.

	Calculated for $Ag_2C_5HBrSO_6.2H_2O$.	Found.
H_2O	6.91	6.97

I. 0.1715 gram of the salt dried at 115° gave, on precipitation with HBr, 0.1340 gram AgBr.

II. 0.1725 gram of the salt dried at 115° gave, on precipitation with HBr, 0.1337 gram AgBr.

III. 0.4347 gram of the salt dried at 115° gave, on heating with HNO_3, 0.1684 gram AgBr and 0.2082 gram $BaSO_4$.

IV. 0.5100 gram of the salt dried at 115° gave, on heating with HNO_3, 0.1980 gram AgBr.

	Calculated for $Ag_2C_5HBrSO_6$.	Found. I.	II.	III.	IV.
Ag	44.54	44.88	44.53		
SO_3	16.50			16.44	
Br	16.50			16.49	16.52

Potassic β-Sulpho-δ-brompyromucate, $K_2C_5HBrSO_6$.—The potassium salt is very soluble in cold water, and crystallises in thick rhombic plates which are anhydrous.

I. 0.4510 gram of the salt gave 0.2247 gram K_2SO_4.

II. 0.5020 gram of the salt gave 0.2530 gram K_2SO_4.

	Calculated for $K_2C_5HBrSO_6$.	Found. I.	II.
K	22.52	22.37	22.62

Action of Bromine.

Bromine in aqueous solution acts with readiness upon β-sulpho-δ-brompyromucic acid or its salts. The products vary with the conditions chosen. If one molecule of bromine is slowly added to a cold aqueous solution of the barium salt, carbonic dioxide is evolved and baric dibromfurfuran sulphonate is formed together with baric bromide. This reaction is obviously identical with that noticed by Hill and Hartshorn[1] in the decomposition of δ-brompyromucic acid in alkaline solution by bromine in which αα-dibromfurfuran is formed. If the baric β-sulpho-δ-brompyromucate is suspended in a little water, and bromine slowly added, the salt at first dissolves, and soon after the baric dibromfurfuran sulphonate crystallises out. From a more dilute solution the salt can readily be obtained by evaporation. In the latter case the solution is but feebly acid and the yield nearly quantitative.

[1] Ber. **18**, 448.

Baric aa-Dibromfurfuran-β-sulphonate, $Ba(C_4HBr_2SO_4)_2.H_2O$. —This salt is quite readily soluble in hot water, more sparingly in cold water, and crystallises in pearly scales or plates.

I. 0.8179 gram of the air-dried salt lost, at 135°, 0.0204 gram H_2O.

II. 0.8833 gram of the air-dried salt lost, at 125°, 0.0224 gram H_2O.

	Calculated for $Ba(C_4HBr_2SO_4)_2.H_2O$.	Found. I.	II.
H_2O	2.35	2.49	2.54

I. 0.3952 gram of the salt dried at 135° gave 0.1238 gram $BaSO_4$.

II. 0.3932 gram of the salt dried at 135° gave 0.1223 gram $BaSO_4$.

III. 0.4219 gram of the salt dried at 125° gave 0.1320 gram $BaSO_4$.

	Calculated for $Ba(C_4HBr_2SO_4)_2$.	Found. I.	II.	III.
Ba	18.40	18.42	18.28	18.40

Potassic aa-Dibromfurfuran-β-sulphonate, $KC_4HBr_2SO_4$. — The potassium salt can readily be made by the action of bromine upon a slightly alkaline solution of potassic β-sulpho-δ-brompyromucate. It crystallises in well formed prisms which are anhydrous.

I. 0.3725 gram of the salt gave 0.4090 gram AgBr, and 0.2540 gram $BaSO_4$.

II. 0.3329 gram of the salt gave 0.3649 gram AgBr, and 0.2283 gram $BaSO_4$.

	Calculated for $KC_4HBr_2SO_4$.	Found. I.	II.
Br	46.49	46.73	46.66
SO_3	23.25	23.41	23.55

Bromine in aqueous solution readily attacks the salts of the *aa*-dibromfurfuran-β-sulphonic acid; so that, if an excess of bromine is added to a salt of β-sulpho-δ-brompyromucic acid, only the products of this second stage of the reaction are obtained. The oxidation goes on slowly at ordinary temperatures, more rapidly on warming, and even after treating for a long time at 100° with an excess of bromine, no appreciable amount of sulphuric acid is formed. The final product of the reaction is an acid containing the sulpho-group, which we have named, provisionally at least, sulphofumaric acid. The acid itself we found to be extremely soluble in water, and upon evaporating the aqueous solution *in vacuo*,

a viscous residue was obtained which did not crystallise even after long standing. The barium, lead, and silver salts of the acid were very sparingly soluble even in boiling water. The calcium and potassium salts, on the other hand, were very soluble even in cold water, and could not be obtained in crystalline form. As might have been expected, the strontium salt proved to be more readily soluble than the barium salt, but it did not crystallise well from water. We also found it impossible to prepare an acid salt the properties of which were more favorable to purification. We therefore prepared and analysed the barium and silver salts.

Baric Sulphofumarate, $Ba_3(C_4HSO_7)_2 . x\ H_2O$.—To an aqueous solution of baric β-sulpho-δ-brompyromucate we added a slight excess of bromine, and finished the reaction by the aid of heat. The strongly acid solution thus obtained was partially neutralised by the addition of baric carbonate, the carbonic dioxide expelled by long boiling, and baric hydrate then added to alkaline reaction. In this way a voluminous flocculent precipitate was thrown down, which was dissolved in boiling dilute hydrochloric acid and reprecipitated by ammonic hydrate. Although the baric sulphofumarate was markedly soluble in a solution of ammonic chloride, the analytical results were more satisfactory than when the salt was again precipitated by baric hydrate. The voluminous precipitate, when thoroughly washed and dried by exposure to the air, formed a light, porous hygroscopic mass, which gave us on analysis varying percentages. The salt dried at 130° gave, however, a constant percentage of barium corresponding to that required by a salt with three molecules of water, and even at 200° one molecule of water appeared to be retained. In each case, however, the ratio between the barium and sulphur was found to be as 3 to 2.

0.6486 gram of the air-dried salt gave, after fusion with Na_2CO_3 and $KClO_3$, 0.4918 gram $BaSO_4$(Ba) and 0.3310 gram $BaSO_4$(SO_3).

	Calculated for $Ba_3(C_4HSO_7)_2.7H_2O$.	Found.
Ba	44.52	44.58
SO_3	17.34	17.52

$$Ba : SO_3 = 2.97 : 2.$$

Here it will be seen that the air-dried salt contained seven molecules of water. This, however, must have been an accidental coincidence, since the same salt after several days further exposure to the air, contained more water.

1.2865 gram of the air-dried salt lost, at 200°, 0.1686 gram H_2O.

	Calculated for $Ba_3(C_4HSO_7)_2.7H_2O$.	Found.
$6H_2O$	11.70	13.10

0.5471 gram of the salt dried at 200° gave 0.4706 gram $BaSO_4$(Ba), and 0.3159 gram $BaSO_4$(SO_3).

	Calculated for $Ba_3(C_4HSO_7)_2.H_2O$.	Found.
Ba	50.42	50.56
SO_3	19.63	19.82

$Ba : SO_3 = 2.98 : 2.$

I. 1.1659 gram of the salt dried at 130° lost, at 200°, 0.0480 gram H_2O.

II. 0.4608 gram of the salt dried at 130° gave 0.3798 gram $BaSO_4$.

III. 0.5175 gram of the salt dried at 130° gave 0.4256 gram $BaSO_4$.

	Calculated for $Ba_3(C_4HSO_7)_2.3H_2O$.	I.	Found. II.	III.
$2H_2O$	4.23	4.12		
Ba	48.29		48.45	48.35

In the sulphuric acid determinations given above, the baric sulphate was precipitated in the presence of large quantities of sodium and potassium salts. Although it was purified in the usual way before weighing, the results are undoubtedly still somewhat too high.

Argentic Sulphofumarate, $Ag_3C_4HSO_7.xH_2O$.—On adding a solution of ammonic sulphofumarate to an excess of argentic nitrate, the silver salt is thrown down as a heavy curdy precipitate, which frequently becomes crystalline on standing. It is very sparingly soluble in cold water, somewhat more readily in hot. The air-dried salt contains water, a part of which at least it loses at 100°. At 110° it loses more rapidly in weight, but decomposition ensues at the same time. A sample of the salt which had been dried for some time at 100°, but which was still losing very slowly in weight, was analysed with the following results:

I. 0.4448 gram of the salt gave 0.4673 gram AgBr, and 0.1933 gram $BaSO_4$.

II. 0.4834 gram of the salt gave 0.2933 gram Ag.

	Calculated for $Ag_3C_4HSO_7.H_2O$.	Found. I.	II.
Ag	60.54	60.39	60.67
SO_3	14.95	14.92	

$Ag : SO_3 = 3.01 : 1.$

The air-dried salt had already lost at 100° about one molecule of water.

1.0317 gram of the air-dried salt lost, at 100°, 0.0368 gram H_2O.

	Calculated for $Ag_2C_4HSO_7.2H_2O$.	Found.
$1H_2O$	3.26	3.57

The air-dried salt, therefore, appeared to contain two molecules of water. The analysis of a second preparation of the air-dried salt gave substantially the same ratio between silver and sulphur, and yet showed that the salt contained a lower percentage of silver.

0.4680 gram of the air-dried salt gave 0.3561 gram AgCl and 0.2009 gram $BaSO_4$.

	Calculated for $Ag_2C_4HSO_7.2H_2O$.	Found.
Ag	58.59	57.28
SO_3	14.46	14.73

$$Ag : SO_3 = 2.88 : 1.$$

By drying over sulphuric acid the precipitated silver salt, we were unable to obtain it with any more definite or constant percentages of water.

The lead salt is almost insoluble in water or in dilute acetic acid; but we have been unable as yet to obtain any results on analysis which were wholly satisfactory.

There can be no doubt that β-sulpho-δ-brompyromucic acid is decomposed by bromine in aqueous solution according to the following equations:

$$C_5H_3BrSO_6 + Br_2 = C_4H_3Br_2SO_4 + CO_2 + HBr.$$
$$C_4H_2Br_2SO_4 + Br_2 + 3H_2O = C_4H_4SO_7 + 4HBr.$$

Action of Nitric Acid.

The decomposition of β-sulpho-δ-brompyromucic acid with nitric acid we have followed qualitatively. We have been unable hitherto to effect a replacement of the sulpho-group by the action of fuming nitric acid, as we had so readily done with the δ-sulphonic acids. In this case, whatever was the strength of the nitric acid, we could only prove the formation of an acid which was identical in its behavior with sulphofumaric acid. Not unfrequently, however, the oxidation had gone further, and oxalic acid was also formed together with sulphuric acid.

We have made a few experiments concerning the action of fusing potassic hydrate upon potassic β-sulpho-∂-brompyromucate, and have as yet been able to prove the formation of nothing but oxalic acid. While it is doubtful whether any other product but oxalic acid is normally formed, we shall study the reaction further, as well as the action of fusing sodic formiate.

β-Sulphopyromucic Acid.

The ammoniacal solution β-sulpho-∂-brompyromucic acid is reduced without difficulty by zinc dust. A strongly ammoniacal solution of the barium salt was heated for some time with an excess of zinc dust, the filtered solution boiled with the addition of baric hydrate till ammonia was no longer given off, and the excess of baric hydrate precipitated with carbonic dioxide. The solution thus obtained yielded on evaporation the barium salt of β-sulphopyromucic acid in satisfactory quantity. Since this salt was very nearly if not quite as soluble in cold water as in hot, its purification could most conveniently be effected by conversion into the acid salt, which was readily soluble in hot water, but sparingly in cold water.

Baric β-Sulphopyromucate, $BaC_5H_2SO_6 . 3\,H_2O$.—This salt is sparingly soluble in hot water, and the hot saturated solution deposits nothing on cooling. By evaporation *in vacuo* over sulphuric acid, the salt is obtained in clear, obliquely terminated plates which contain three molecules of water.

I. 1.5356 gram of the air-dried salt lost, at 160°, 0.2156 gram H_2O.

II. 1.2179 gram of the air-dried salt lost, at 160°, 0.1707 gram H_2O.

III. 0.7448 gram of the air-dried salt gave 0.4571 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6.3H_2O$.	Found. I.	II.	III.
H_2O	14.18	14.05	14.02	
Ba	35.96			36.08

I. 0.7139 gram of the salt dried at 160° gave 0.5092 gram $BaSO_4$.

II. 0.7303 gram of the salt dried at 160° gave 0.5197 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_6$.	Found. I.	II.
Ba	41.90	41.94	41.84

If the solution is evaporated at 100°, the salt separates in small clear prisms with oblique truncations, which appear to contain one molecule of water.[1] If the salt is removed while the solution is hot, it contains a somewhat lower percentage of water (IV) than it does when the solution is first allowed to cool (I, II, and III). In the latter case it undoubtedly contains a slight admixture of the salt containing three molecules of water.

I. 4.2755 grams of the air-dried salt lost, at 165°, 0.2510 gram H_2O.

II. 2.1345 grams of the air-dried salt lost, at 165°, 0.1290 gram H_2O.

III. 0.5901 gram of the air-dried salt gave 0.3981 gram $BaSO_4$.

IV. 0.8840 gram of the air-dried salt lost, at 160°, 0.0484 gram H_2O.

	Calculated for $BaC_5H_2SO_4.H_2O$.	Found. I.	II.	III.	IV.
H_2O	5.22	5.87	6.04		5.47
Ba	39.71			39.66	

I. 0.6005 gram of the salt dried at 165° gave 0.4270 gram $BaSO_4$.

II. 0.6010 gram of the salt dried at 165° gave 0.4269 gram $BaSO_4$.

	Calculated for $BaC_5H_2SO_4$.	Found. I.	II.
Ba	41.90	41.79	41.76

In determining the solubility of the barium salt in cold water, we evaporated its solution rapidly until crystals began to appear, and then cooled with constant stirring. Abundant crystals of the salt were thus formed. In order to satisfy ourselves that solutions of constant composition could be obtained in this way, we made four separate determinations.

I. 16.2601 grams of the solution saturated at 21° gave 0.2172 gram $BaSO_4$.

II. 14.4321 grams of the solution saturated at 21° gave 0.1950 gram $BaSO_4$.

III. 12.1256 grams of the solution saturated at 21° gave 0.1646 gram $BaSO_4$.

IV. 12.7701 grams of the solution saturated at 21° gave 0.1788 gram $BaSO_4$.

The aqueous solution of barium salt saturated at 21°, therefore, contained the following percentages of the anhydrous salt:

[1] In a preliminary paper (Ber. **18**, 2095) the baric β-sulphopyromucate was described as containing but one molecule of water. At that time the salt obtained by evaporation at 100° had alone been analysed.

I.	II.	III.	IV.
1.88	1.90	1.91	1.96

Acid Baric β-Sulphopyromucate, $Ba(C_5H_2SO_6)_2 . 3H_2O$.—This salt may be made by dissolving the neutral barium salt in hydrochloric acid, or, more advantageously, by mixing solutions of the neutral barium salt and the free acid in equivalent quantities. It is readily soluble in hot water, more sparingly in cold water, and crystallises in small, obliquely truncated prisms which are permanent in the air.

I. 1.4255 gram of the air-dried salt lost, at 130°, 0.1403 gram H_2O.

II. 1.3386 gram of the air-dried salt lost, at 135°, 0.1271 gram H_2O.

III. 0.5371 gram of the air-dried salt gave 0.2193 gram $BaSO_4$.

	Calculated for $Ba(C_5H_2SO_6)_2.3H_2O$.	Found. I.	II.	III.
H_2O	9.42	9.84	9.49	
Ba	23.91			24.00

I. 0.3068 gram of the anhydrous salt gave 0.1378 gram $BaSO_4$.

II. 0.3128 gram of the anhydrous salt gave 0.1409 gram $BaSO_4$.

	Calculated for $Ba(C_5H_2SO_6)_2$.	Found. I.	II.
Ba	26.39	26.41	26.48

Calcic β-Sulphopyromucate, $CaC_5H_2SO_6.2H_2O$.—The calcium salt is quite readily soluble in cold water, and separates on evaporation in crusts. By the addition of alcohol to a cold aqueous solution the salt is precipitated in the form of small prisms, which, when dried by exposure to the air, contain two molecules of water.

I. 1.0454 gram of the air-dried salt lost, at 130°, 0.1444 gram H_2O.

II. 1.0285 gram of the air-dried salt lost, at 135°, 0.1415 gram H_2O.

	Calculated for $CaC_5H_2SO_6.2H_2O$.	Found. I.	II.
H_2O	13.53	13.81	13.74

I. 0.4790 gram of the anhydrous salt gave 0.2825 gram $CaSO_4$.

II. 0.4118 gram of the anhydrous salt gave 0.2425 gram $CaSO_4$.

	Calculated for $CaC_5H_2SO_6$.	Found. I.	II.
Ca	17.40	17.35	17.32

Potassic β-Sulphopyromucate, $K_2C_5H_2SO_6.2\frac{1}{2}H_2O$.—The potassium salt is extremely soluble in water, and crystallises in long prisms. It separates in the form of fine needles on the addition of alcohol to its aqueous solution.

1.2358 gram of the air-dried salt lost, at 140°, 0.1788 gram H_2O.

	Calculated for $K_2C_5H_2SO_6.2\frac{1}{2}H_2O$.	Found.
H_2O	14.37	14.47

I. 0.4028 gram of the salt dried at 140° gave 0.2601 gram K_2SO_4.

II. 0.4120 gram of the salt dried at 140° gave 0.2665 gram K_2SO_4.

	Calculated for $K_2C_5H_2SO_6$.	Found. I.	Found. II.
K_2	29.16	28.99	29.04

Action of Bromine.

We have as yet made but few experiments as to the action of bromine in aqueous solution upon β-sulphopyromucic acid. They have only been sufficient to show that oxidation here follows the same course that it does in the case of other derivatives of pyromucic acid in which the δ-hydrogen atom is unreplaced. At first products are formed which reduce silver energetically in ammoniacal solution; and only after long warming with an excess of bromine is an acid obtained which resembles in its behavior sulphofumaric acid. Three molecules of bromine gave an acid whose barium salt was very readily soluble in water, and which reduced silver on heating. This reaction will be studied more carefully hereafter, with the hope of isolating the aldehyde acid which is doubtless formed.

Action of Fuming Sulphuric Acid upon βδ-Dibrompyromucic Acid.

By the action of fuming sulphuric acid upon δ-brompyromucic acid, we obtained a sulphonic acid which of necessity contained its sulpho-group either in the β or in the γ position. Analogy left little room for doubt that the acid thus formed was in fact a β-sulphonic acid. It seemed to us not impossible that a γ-sulphonic acid could be formed by the action of fuming sulphuric acid upon

$\beta\delta$-dibrompyromucic acid, which still retains its γ-hydrogen atom. We found, however, that the reaction takes quite a different course, and that no sulphonic acid is formed.

Pure dry $\beta\delta$-dibrompyromucic acid, melting at 167°–168°, was slowly added to several times its weight of fuming sulphuric acid. No visible reaction took place, and after twenty-four hours standing, water precipitated the acid apparently quite unchanged. After the lapse of several days decomposition set in, and carbonic dioxide, bromine, hydrobromic acid, and sulphurous dioxide were evolved. So slow was the reaction that two or three weeks were necessary for its completion at ordinary temperatures. When water gave only a slight flocculent precipitate, the bromine was expelled as far as possible with a current of air, and the whole diluted with water. The small quantity of insoluble matter was then removed by filtration, and the aqueous solution thoroughly extracted with ether. The ether left on distillation a white crystalline acid which, when pressed and dried, melted at 127°–128°. The quantity of the acid thus obtained was about half that of the $\beta\delta$-dibrompyromucic acid taken. The acid dissolved readily in less than its own weight of water, leaving but the slightest turbidity, and on evaporation it crystallised in colorless prisms which melted at 129°–130°.[1] An analysis showed this substance to be monobrommaleic acid.

0.2235 gram of the acid dried over sulphuric acid gave 0.2161 gram AgBr.

Calculated for $C_4H_3BrO_4$.	Found.
41.03	41.15

[1] The melting point of monobrommaleic acid is usually given as 128°, and I have frequently determined it myself without noticing that it varies greatly with the time of heating, as is the case with dibrommaleic acid. How great this variation may be can be seen from the following observations, which I made with this one analysed sample. The acid in thin-walled capillary tubes was dipped into the bath heated to constant temperature, and the time of melting noted.

Temperature of bath.	Minutes before melting.
143°	0 17
140	0.5
135	0.83
133	1.3
131	1.5
125	4.5
121	8.0

The melting point, 129°–130°, given above was the result of two successive attempts to determine it at the ordinary speed.—H. B. H.

The melting point and the complete and ready solubility of the crude product showed that monobrommaleic was the only essential constituent. The aqueous solution from which the monobrommaleic acid had been extracted with ether was warmed to expel the ether dissolved, neutralised with baric carbonate, and the filtered solution evaporated. A careful examination of the small amount of barium salt thus obtained failed to show that even a trace of a sulphonic acid had been formed.[1] This result is in accordance with the results of Hill and Sanger,[2] who found that the γ-hydrogen of the $\beta\delta$-dibrompyromucic acid could not be replaced by bromine.

Action of Fuming Sulphuric Acid upon Tribrompyromucic Acid.

After the experiments just described, there could be little doubt as to the action of fuming sulphuric acid upon tribrompyromucic acid. We thought it worth while, however, to make a single experiment in this direction. Tribrompyromucic acid dissolved readily in fuming sulphuric acid, and decomposition quickly ensued at ordinary temperatures, so that the reaction was completed in the course of a day or two. The diluted solution yielded, as the only product of the reaction, dibrommaleic acid, which we recognised by the melting point of its anhydride (114°–115°), and by the analysis of its barium salt.

0.5812 gram of the air-dried salt gave 0.3063 gram $BaSO_4$.

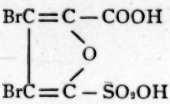
	Calculated for $BaC_4Br_2O_4.2H_2O$.	Found.
Ba	31.78	31.98

Theoretical Considerations.

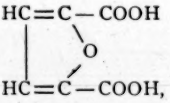
The constitution of the various substances described in the preceding pages requires but little discussion. The position of the sulpho-group in the δ-sulphopyromucic acid is established not only by the formation of fumaric acid by its oxidation, but also still more conclusively by its formation in the reduction of $\beta\gamma$-dibrom-δ-sulphopyromucic acid, to which of necessity the formula

[1] The statement made in a preliminary paper (Ber. **18**, 2095), that a sulphonic acid was formed in this reaction, was subsequently proved to be incorrect.

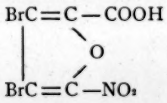
[2] Proceedings, Amer. Acad. **21**, 175.

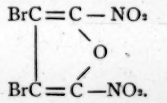


must be assigned. The close resemblance in structure of this acid to dehydromucic acid,

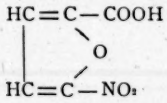


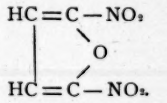
is evident, and the formation of δ-nitropyromucic acid from dehydromucic acid as observed by Klinkhardt,[1] finds its complete parallel in the conversion of this sulphonic acid by the action of nitric acid into $\beta\gamma$-dibrom-δ-nitropyromucic acid and $\alpha\alpha$-dinitro-$\beta\beta$-dibromfurfuran.



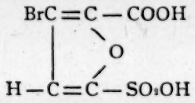


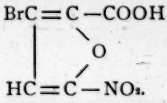
There can be no doubt that the neutral substance formed by the action of fuming nitric acid upon δ-sulphopyromucic acid at the same time with the δ-nitropyromucic acid is $\alpha\alpha$-dinitrofurfuran.





The structure of the β-brom-δ-sulphopyromucic acid is determided by its reduction to δ-sulphopyromucic acid, and by its formation from β-brompyromucic acid, the constitution of which has been established by Hill and Sanger.[2] The sulphonic acid and the nitro-acid formed from it must be

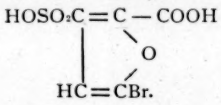




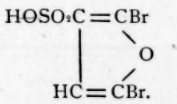
[1] J. prakt. Chem. N. F. **25**, 41.

[2] Proceedings, Amer. Acad. **21**, 181.

Concerning the structure of the sulphonic acid formed from ∂-brompyromucic acid, it is impossible to draw conclusions equally definite. When we bear in mind, however, the fact that bromine, like sulphuric acid, first replaces the ∂-hydrogen atom of the pyromucic acid, and in acting upon the ∂-brompyromucic acid thus formed the β-hydrogen alone can further be replaced by bromine, there seems no reasonable doubt that the sulphuric acid in acting upon ∂-brompyromucic acid also replaces by the sulpho-group the β-hydrogen atom. This view is still further confirmed by the fact that the γ-hydrogen atom of the $\beta\partial$-dibrompyromucic acid seems incapable of such replacement. If this view be correct, the sulphonic acid in question has the form



In any case, the $\alpha\alpha$-dibromfurfuran-β-sulphonic acid formed from it by the action of bromine has the structure



ON THE OCCURRENCE OF ARSENIC IN GLASS AND IN THE CAUSTIC ALKALIES,

With an Examination of the Action of the Strong Acids, Caustic Alkalies, and Other Reagents, upon Arsenical Glass.

By John Marshall and Charles S. Potts.

Over forty years ago the Academy of Medicine of Paris, at the request of the French Government, undertook the investigation of the occurrence of arsenic in glass, and as a result of the research declared that "the glass which they examined contained no arsenic, and although arsenic is sometimes used in glassmaking, and a

trace of it may be retained in some opaque glasses or enamels, it cannot be detected by any process of analysis in any of the clear glass met with in commerce, *all of the arsenic being volatilised* during the manufacture of the glass."[1]

It is well known that arsenious oxide is extensively used in the manufacture of glass, principally to decompose the sodium sulphide formed in the process,[2] and also to effect the removal of color from the glass mixture containing carbon or silicate of iron. The arsenious oxide is reduced to the metallic form by the carbon and ferrous oxide at a dull red heat, and according to Wagner[3] and others, the *arsenic is volatilised.* Further on, however, Wagner (p. 392) states that in the use of arsenic in glassmaking, it should not be overlooked that a small portion of the arsenic remains in the finished glass as calcium arsenite or arseniate.

For some years past the presence of traces of arsenic in glass has been admitted. Lately, W. Fresenius[4] has determined it to be present in considerable quantity in some samples of Bohemian glass tubing, such as is used in many laboratory operations. In one of the three samples he found as much as 0.2 per cent. of arsenic. Again, M. Kreusler[5] found in a sample of Thuringian glass 0.15 per cent. of As_2O_5. In a sample of Bohemian combustion tubing the same investigator found 0.12 per cent. of As_2O_5, and in an easily fusible potash glass 0.10 per cent. of As_2O_5. The finding of arsenic in such quantity disproves the old belief that *all the arsenic is volatilised.* Upon inquiry at a glass bottle manufactory in Philadelphia, it was learned that in the process employed in the establishment, approximately twenty pounds of arsenious oxide were used to each melting of four thousand pounds of glass, and in making clear glass the pots were kept closed with a lid, thus in a measure preventing the escape of any arsenic that might volatilise.

The following investigation was begun primarily to determine the presence of arsenic in glass of American manufacture, but its scope was somewhat enlarged and glass of foreign make was included. The action of the caustic alkalies, strong acids, and ordinary laboratory reagents, upon the arsenical glass of the bottles in which they were contained, was also studied. The occurrence of arsenic in commercial caustic soda, sodium carbonate, and also

[1] Annales d'Hyg. Pub. et de Med. **11**, 224.
[2] Post. Chemische Technologie **2**, 17.
[3] Handbuch d. chem. Tech. 1886, 392.
[4] Ztschr. anal. Chem. **22**, 397.
[5] Wagner, Handbuch d. chem. Tech. 1886, 386.

in sodium hydrate and sodium carbonate sold as chemically pure, was investigated. In every case the presence of arsenic was first determined qualitatively by Marsh's test, and when found, a quantitative determination followed. In examining the glass for arsenic the following method was employed: The glass was pulverised in an agate mortar, then mixed with sodium carbonate, and fused. The fused mass was broken up and dissolved in water, then acidified with sulphuric acid, the separated silica filtered off, and the filtrate placed in the Marsh apparatus.

The reagents employed, sodium carbonate, sulphuric acid, and zinc, were tested in long continued control experiments and found to be perfectly free from arsenic. Lead was found in some of the samples of glass, but no quantitative determinations were made.

In the quantitative estimations the glass was pulverised as before and fused with sodium carbonate. The fused mass was broken up, dissolved in water, and acidified with sulphuric acid. The silica was filtered off, and the filtrate, to which had been added a solution of sulphurous acid gas, was evaporated to a small volume on a water-bath, and then diluted with a little hot water and filtered from the remaining separated silica. Through the warm filtrate a washed stream of hydrogen sulphide was passed for several hours, and the precipitated arsenious sulphide collected on a filter paper and washed. The precipitate was then dissolved, while on the filter, with a few drops of dilute ammonium hydrate, the solution evaporated to dryness, and the residue warmed with strong nitric acid until the sulphide was completely oxidised. The acid was driven off by evaporation to dryness, and the residue was warmed with a little water and then filtered. Magnesium mixture was added to the filtrate and the whole allowed to stand twenty-four hours. The precipitated magnesium ammonium arseniate was collected on a filter paper and the arsenic weighed as magnesium pyro-arseniate.

	Quantity of glass employed.	Description.	Where made.	Amount of $Mg_2As_2O_7$ obtained.	Equivalent percentage of As_2O_3.
I	5.0 grams	8-liter bottle	Germany	0.010	0.127
II	5.0 "	Reagent bottle	Philadelphia	0.015	0.191
III	5.0 "	Beaker	"	0.024	0.306
IV	2.0 "	Reagent bottle	"	0.008	0.255
V	2.0 "	Refractory tubing	Thuringia	0.003	0.095
VI	5.0 "	8-liter bottle	Germany	0.008	0.102
VII	5.0 "	Beaker	Philadelphia	0.035	0.446

When glass tubing No. 5, which contained arsenic, but no lead, was used as a reduction tube and pure hydrogen passed through in Marsh's test, the brown coloration referred to by Fresenius[1] as produced directly at the point in contact with the flame invariably appeared.

Examination of the Caustic Alkalies, the Strong Acids and other Reagents, for the Presence of Arsenic, and Investigation of their Solvent Action upon the Arsenical Glass of the Bottles in which they were contained.

In testing the alkalies, sulphuric acid was used for acidifying. The strong acids were sufficiently diluted with distilled water, or partly neutralised with sodium carbonate before testing.

In all but one of the samples of caustic soda examined, arsenic was found, varying from a trace to quite a considerable percentage. Four samples of caustic potash were examined, but no arsenic was detected.

Qualitative.

I. Two samples, each containing twenty grams of sodium carbonate, sold as chemically pure and obtained from different German makers, separately neutralised with sulphuric acid and tested in Marsh's apparatus, gave different results. One sample furnished a very slight mirror, the other gave no indication of the presence of arsenic.

II. Ten grams of sodium hydrate, in sticks made in Philadelphia, gave a slight mirror. These sticks were contained in an arsenical glass bottle, so that care was taken to select the sticks not in direct contact with the glass. The end in contact with the bottom or side of the bottle was broken off and rejected.

III. Ten grams of caustic soda, made by the Solvay process, failed to show the presence of arsenic.

Quantitative.

In estimating the quantity of arsenic in the alkalies, they were dissolved in water, then rendered slightly acid with sulphuric acid, sulphurous acid added, and the latter driven off by heating the liquid. Hydrogen sulphide was passed through the solution, the precipitated arsenious sulphide was collected on a filter, washed,

[1] Ztschr. anal. Chem. **22**, 400.

dissolved in ammonium hydroxide, the solution evaporated to dryness, and the residue of arsenious sulphide oxidised with nitric acid. The nitric acid was driven off by heat, the residue dissolved in water, filtered, magnesium mixture added to the filtrate, the precipitate was collected on a filter, and the arsenic weighed as pyro-arseniate.

I. One hundred grams of sodium hydrate in sticks, made by a Philadelphia firm, furnished 0.0044 gram of $Mg_2As_2O_7$, equivalent to 0.0028 per cent. of As_2O_3.

II. Three grams of a very white caustic soda, sold as chemically pure, gave 0.004 gram of $Mg_2As_2O_7$, equivalent to 0.0848 per cent. of As_2O_3.

III. Ten grams of another sample of white caustic soda, represented to be chemically pure, yielded 0.0062 gram of $Mg_2As_2O_7$, equivalent to 0.039 per cent. of As_2O_3.

IV. Twenty grams of a sample of "crude carbonated soda," made in England, furnished 0.021 gram of $Mg_2As_2O_7$, equivalent to 0.067 per cent. of As_2O_3.

In order to study the solvent action of caustic soda upon glass, bottles of arsenical glass of about 500 cc. capacity were filled with a 10 per cent. solution of sodium hydroxide (free from arsenic) and allowed to stand different periods of time.

I. 20 cc. of the solution which had been allowed to stand in a bottle five months, when tested with Marsh's test, produced a very strong mirror in six minutes.

II. 20 cc. of the solution contained in a bottle one month gave a decided mirror in ten minutes.

III. 20 cc. of the solution which had been kept in a bottle twenty-three hours gave no reaction. Twenty cubic centimetres of this solution were tested after the lapse of every twenty-three hours, and no arsenical mirror appeared until the sixty-ninth hour.

IV. 20 cc. of a 10 per cent. solution of potassium hydroxide kept in a bottle twenty-four hours readily produced an arsenical mirror.

The strong acids, sulphuric and hydrochloric, which were examined had been kept in large (eight-liter) arsenical glass bottles for different lengths of time. The bottles being of large size, quite an extensive surface of glass was exposed to the action of the acid. The acids, previously neutralised with sodium carbonate (free from arsenic), were tested in Marsh's apparatus.

I. 40 cc. of strong hydrochloric acid (American), kept in an arsenical glass bottle three months, gave no trace of arsenic.

II. 40 cc. of strong hydrochloric acid (German), contained in an arsenical glass bottle three years, failed to give a trace of arsenic. The glass of the bottle in which this acid was kept contained 0.102 per cent. of As_2O_3.

III. 40 cc. of strong sulphuric acid (American), contained in an arsenical glass bottle three months, did not give a trace of arsenic.

IV. 40 cc. strong sulphuric acid (German), contained in an arsenical glass bottle six years, failed to give any indication of arsenic. The glass of this bottle contained 0.127 per cent. of As_2O_3.

Some of the ordinary laboratory reagents kept in arsenical glass bottles were tested with Marsh's test, but, as shown below, failed to give any indication of the presence of arsenic.

Two samples, 50 cc. each, of ammonium hydroxide, kept respectively one and two months, failed to show arsenic. Solutions of potassium nitrate and chlorate and a strong solution of barium chloride kept in arsenical glass bottles, failed to produce a mirror.

Sodium carbonate, which originally contained arsenic, was after several recrystallisations found to be entirely free from the metal.

It will be observed that every sample of clear glass examined except one, and all the caustic soda except one sample (that made by the Solvay process), contained arsenic. The caustic potash, ammonium hydroxide, and the common reagents examined were found to be free from arsenic. The strong acids, ammonium hydroxide, and ordinary reagents had no dissolving action upon the surface of arsenical glass bottles, whereas solutions of the fixed alkalies had such solvent action.

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NOTE ON THE BUTINES.

BY L. M. NORTON AND A. A. NOYES.

There are certainly four possible hydrocarbons of the composition C_4H_6: dimethylacetylene, $CH_3—C\equiv C—CH_3$; ethylacetylene, $CH\equiv C—C_2H_5$; vinylethylene, $CH_2=CH—CH=CH_2$; and methylisoallylene, $CH_2—CH=C=CH_2$. The first three of these have already been prepared. Vinylethylene was first obtained by

Caventou[1] in 1863, by the action of heat on amyl alcohol, and it has since been many times prepared by numerous other investigators. Its production from erythrite by reduction,[2] the identity of its tetrachloride with that prepared by the action of phosphorus pentachloride on erythrite,[3] and its oxidation to formic acid,[4] fully establish its constitution. Ethylacetylene was first obtained by Bruylants[5] in 1875, from methylethyldichlormethane and alcoholic potash. Its behavior toward ammoniacal cuprous and silver solutions shows it to be a derivative of acetylene formed by the replacement of only one hydrogen atom. Dimethylacetylene has been prepared by Lermontoff by the action of alcoholic potash on pseudo-butylene bromide, and treatment of the brombutylene obtained with sodium ethylate; for by contact with sulphuric acid, the butine so prepared polymerises to hexamethylbenzene.[6] The fourth butine, methylisoallylene, was the subject of this investigation.

The method used for its preparation consisted in the reduction of butyric chloral, $CH_3 - CHCl - CCl_2 - CHO$, to the corresponding alcohol by addition of zinc ethyl, and subsequent decomposition of the zinc compound by water as recommended by Garzarolli.[7] The hydroxyl of this alcohol was then replaced by chlorine by means of phosphorus pentachloride, giving methylisoallylene tetrachloride, $CH_3 - CHCl - CCl_2 - CH_2Cl$, from which, to obtain the butine, it was only necessary to remove the chlorine by the action of the zinc-copper couple and alcohol. That the butyric chloral has the constitution assigned to it above has been proved by Friedrich,[8] who showed the identity of the reduction product of its corresponding acid with α-chlorcrotonic acid, and by Lieben and Zeisel,[9] who prepared it by the condensation of aldehyde with chloraldehyde, and who found that the dichlorpropylene split from it by caustic potash gave acetic acid on oxidation. That the atoms undergo no change in position in the reduction of the chloral to trichlorbutyl alcohol is evident, since both these substances give the same trichlorbutyric acid on oxidation.[10]

The butyric chloral used was obtained from commercial croton

[1] C. R. **56**, 646, 712.
[2] Henninger, Bull. Soc. chim. [2] **19**, 145; Ciamician and Magnaghi, Ber. **19**, 569.
[3] Henninger, Bull. Soc. chim. [2] **34**, 195.
[4] Armstrong and Miller, J. Chem. Soc. **49**, 82.
[5] Ber. **8**, 412.
[6] Almedingen, Ber. **14**, 2073.
[7] Ann. Chem. (Liebig) **213**, 369.
[8] Ann. Chem. (Liebig) **219**, 371.
[9] Monatsh. Chem. **4**, 531.
[10] Ann. Chem. (Liebig) **213**, 374.

chloral hydrate by distillation with sulphuric acid, and subsequent rectification over quicklime. It boiled from 163° to 167°. This was slowly added, in calculated quantity, to a mixture of equal parts of ether and zinc ethyl, placed in a flask filled with carbonic acid, and sealed by a delivery tube dipping under mercury. The temperature was not allowed to rise above that of the room. After the chloral was all added, the flask was allowed to stand for some hours, in order that the action might become complete, and the zinc compound was then decomposed by addition, in small portions, to water acidified with hydrochloric acid. A colorless oil was thus obtained which solidified after standing a short time. The trichlorbutyl alcohol crystallised from ether in large monoclinic prisms; it melted at 57° after one crystallisation. A yield of 60 to 70 per cent. was the result in several experiments.

The trichlorbutyl alcohol was now heated for several hours on a sand-bath in a flask provided with a return cooler with a slight excess of phosphorus pentachloride. The product was treated with water to remove the chlorides of phosphorus, distilled with steam, dried with calcium chloride and fractionated under reduced pressure. In this way methylisoallylene tetrachloride was obtained as a colorless liquid identical in properties with that prepared by Garzarolli in the same way. Cooled to —15° it showed no signs of solidification. The yield in four different cases was between 30 and 40 per cent.

The small yield in methylisoallylene tetrachloride is explained by the formation of a considerable quantity of $\alpha_2\beta$-trichlorbutyl phosphate by the action of phosphorus oxychloride on the alcohol. This substance remained in the flask as a gelatinous mass on distilling with steam, and was purified by repeated crystallisations from alcohol. It separated from this solvent on spontaneous evaporation in slender colorless needles, which unite to radiated tufts if the crystallisation is rapid. The melting point is 85.3° to 85.4°. It gave the following results on analysis:

	Found.	Calculated for $(C_4H_6Cl_3O)_3PO$.
Carbon	24.39	24.98
Hydrogen	3.25	3.12
Chlorine	55.73	55.42
Phosphorus	4.91	5.38

In order to separate the chlorine from methylisoallylene tetrachloride, the latter was mixed in a flask with an equal volume of

alcohol, and the calculated quantity of the zinc-copper couple added.[1] The action begins of itself and must be checked by cooling the flask. The butine, after passing through a return cooler surrounded by water at 30°, was condensed by means of a mixture of ice and salt. It was entirely freed from alcohol by several fractionations. The yield is quite satisfactory.

Methylisoallylene is a colorless liquid, having the characteristic alliaceous odor of the hydrocarbons of the acetylene series. It boils constantly at 18°–19°. It gives no precipitate with ammoniacal cuprous chloride solution. The relation of carbon to hydrogen was found by combustion as follows:

	Found. I.	II.	Calculated for C_4H_6.
Carbon	88.58	88.52	88.89
Hydrogen	11.42	11.48	11.11

Methylisoallylene unites with bromine, giving a liquid dibromide, which, however, takes up more bromine quite rapidly at the ordinary temperature, and therefore was not prepared in a state of purity. The tetrabromide, unlike those of vinylethylene and ethylacetylene, is a colorless liquid, which on cooling to —17° becomes less fluid but does not solidify.

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Contributions from the Chemical Laboratory of Vanderbilt University.

I.—SOME MODIFICATIONS OF THE METHODS OF ORGANIC ANALYSIS BY COMBUSTION.

BY WM. L. DUDLEY.

The investigations recorded here were undertaken with the hope that the method of ultimate organic analysis by combustion might be so modified as to be more rapid and none the less accurate.

The time required in preparation for the combustion by ordi-

[1] Gladstone and Tribe, J. Chem. Soc. **27**, 406. Armstrong and Miller, J. Chem. Soc. **49**, 82.

nary methods is much greater than that for the operation itself; it being consumed in drying and mixing materials, filling and heating up the tube, and in case several combustions are to be made at once, the time required in cooling the tube is very considerable. Then again the liability of loss by breaking the tube in heating and cooling is of no little importance.

The method of burning the substance with a current of air or oxygen in a glass combustion tube containing copper oxide is well known. It is stated, however, without satisfactory reason,[1] that the discrepancy in the hydrogen determination is as great in this method as in that where the substance and copper oxide are mixed, even though in the former the copper oxide is kept hot and the substance introduced in a boat. Kopfer[2] has described a method in which he employs platinum-black mixed with freshly ignited asbestos, instead of copper oxide; and to prevent the gases from passing through the tube without decomposition, he interposes three plugs of asbestos wound with fine platinum wire. The method is said to give very accurate results under careful management.

The platinum combustion tube which is being so generally used in carbon determinations in iron, has, as far as I am aware, never before been used in organic analysis, and the method which I shall describe here can be used with a glass as well as a platinum tube, although the description will be confined to the latter, as it is much preferred. Fig. 1 shows a section of the platinum tube which is

FIG. 1.

used in this laboratory, the main body of which is 48.5 cm. long and 1.5 cm. in diameter. The tail *D* is 13 cm. long and 0.5 cm. in diameter. The tube is filled from one third to one half full with manganese oxide in a coarse granulated condition, several lumps, too large to pass through the tail *D*, being put in first. The manganese oxide is prepared as follows: Manganous carbonate is decomposed with moderately dilute nitric acid in the cold, and evaporated to dryness. The residue is heated to redness over a blast lamp until all of the nitrate is decomposed. The mass, which is for the most part the oxide Mn_3O_4, is cooled and easily granu-

[1] Lieben, Ann. Chem. (Liebig), **187**, 142.

[2] J. Chem. Soc. **29**, 660.

lated to any degree of fineness. No channel is left in the tube, as the manganese oxide should be coarse enough to allow the products of combustion to pass with sufficient freedom. If a glass tube be used, a slight channel should be left. The substance is introduced in a porcelain or platinum boat[1] *B*, and followed by a roll of platinum gauze *C*, 3.5 cm. long, which has a loop in front so that it can be easily withdrawn. At *E* a gas-tight brass coupling is inserted; this carries a tube 0.5 cm. in diameter, to which is connected the apparatus furnishing either air or oxygen as desired.

Instead of the size of the tube being reduced to 0.5 cm. in the tail *D*, Fig. 1, the design shown in Fig. 2 is proposed to facilitate the passage of the water into the calcium chloride tube. The tube *B* is only slightly smaller than the main body, and the end is closed with a stopper carrying the stem of the calcium chloride tube. At *A* is placed a platinum basket to retain the manganese oxide.

FIG. 2.

The whole plan of the apparatus is shown in Fig. 3. Before introducing the substance, and connecting the calcium chloride tube and potash bulb, the portion of the tube containing the manganese oxide is heated to full redness and a rapid current of dry

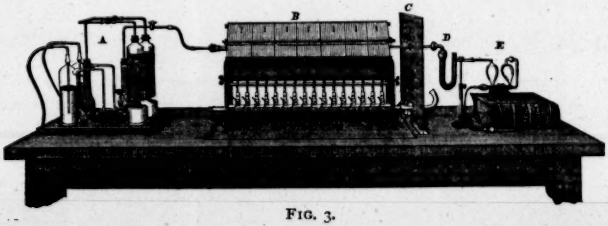


FIG. 3.

and pure air is passed through. The burners are shut off, except the last two or three, which are sufficient to keep about two inches of the tube red hot. The current of air is then stopped and the calcium chloride tube and potash bulbs are attached, and finally the substance is introduced in a platinum or porcelain boat (by

[1] A porcelain boat is preferred in most cases, as the substance burns more uniformly in it than in a platinum boat.

removing the coupling at the posterior end) followed by the roll of platinum gauze. A slow current of air is then turned on, it having been purified by passing through the apparatus shown at *A*, Fig. 3, containing, 1st, a strong solution of caustic potash; 2d, pumice and sulphuric acid, and, 3d, solid caustic potash. Two burners under the portion of the tube containing the roll of platinum gauze are now lighted, and the substance is gradually approached by lighting the burners under the manganese oxide. The red-hot platinum gauze will decompose any condensable gases which may diffuse back, if the combustion should proceed a little too rapidly, and prevent a deposit in the posterior portion of the tube outside of the furnace. An asbestos shield *C*, Fig. 3, protects the calcium chloride tube and potash bulbs from the heat of the furnace.

I prefer to use a Geissler potash bulb with tube for solid potash attached, in which case the air or oxygen may be forced in at the rate of two or three bubbles a second. It is also desirable to use a slight exhaust as well as pressure.

When all of the burners have been lighted, the air is replaced by a current of oxygen, which is continued for about fifteen minutes, when the combustion will have been completed. The burners are then all turned off excepting the three at the end under the manganese oxide, and the bulbs are disconnected and set aside to cool. In a few minutes the platinum gauze may best be removed with a bent wire, and if a second set of bulbs be ready, another combustion may proceed at once. In this way a combustion may be made easily every hour, the actual time consumed in burning the substance being from thirty to forty minutes.

The manganese oxide is regenerated by the oxygen which is passed in during each combustion; it is never reduced below MnO and therefore can do the platinum tube no damage. We have a platinum tube in which over fifty combustions were made during two months without removing the manganese oxide, and on examination afterward, the inside of the tube was found to be as clean and sound as ever.

As for the accuracy of the method, I will simply give five results of the analyses of sugar made by Mr. L. M. Donaldson under my direction:

No.	Carbon.	Hydrogen.
1.	42.00	6.62
2.	42.20	6.52
3.	42.02	6.56
4.	42.08	6.55
5.	42.07	6.24
Mean,	42.07	6.49
Theory,	42.10	6.44
Error,	—.03	+.05

I also give five results obtained by him by the same method, using a glass tube instead of platinum. They are as follows:

No.	Carbon.	Hydrogen.
1.	41.90	6.43
2.	41.92	6.37
3.	42.05	6.41
4.	42.24	6.36
5.	41.99	6.37
Mean,	42.02	6.39
Theory,	42.10	6.44
Error,	—.08	—.05

The method of carrying on the combustion of liquids of high boiling point is similar to that for solids. The required amount of liquid is placed in the boat and the combustion proceeded with as before, except in most cases it is best to approach the substance with the heat a trifle more slowly. For convenience in weighing and handling such liquids, I have used the arrangement shown in Fig. 4. It consists simply of a thin glass bottle with a stopper *B*, through which passes a tube *C*, reaching to the bottom. *A* is rubber bulb attached to the end of the tube, forming an ordinary liquid dropper. The bottle containing the liquid is weighed, and after the requisite amount of the substance for combustion has been transferred to the boat by means of the dropper, the whole is weighed again.

FIG. 4.

In the case of very volatile liquids, the following method is employed: The volatile liquid is drawn into the bulb *A*, about 3.5 cm. in diameter, shown in Fig. 5, and the whole weighed. The bulb is then connected by the limb *D* to the combustion tube, and by the other to the purifying apparatus *A*, Fig. 3. The combustion tube is filled three-fourths full of manganese oxide, and

heated to redness before the bulb containing the liquid is attached; the calcium chloride and potash bulbs are also previously connected. A slow current of nitrogen is then passed through the apparatus to serve simply as a carrier of the vapor of the substance, and to avoid danger of explosion, which would exist if oxygen or air was employed for the same purpose. A few inches below the bulb *A*, Fig. 5, is placed an iron plate *B*, of sufficient size to evenly distribute the heat, which is furnished by the lamp *C*, through the bulb and connecting tubes, so as to prevent the condensation of the liquid *en route* to the combustion tube. The temperature of the plate should be so regulated as to rapidly evaporate the liquid in the bulb, but without boiling it. After all of the liquid has left the bulb and passed into the combustion tube, the current of nitrogen is cut off, and air or oxygen is turned on. The latter is always preferred. The use of nitrogen in no way interferes with the combustion of the substance, and the absorption of it by the potash bulb is not materially appreciable in the results. The nitrogen may be prepared sufficiently pure by passing air over red hot copper in a porcelain tube, and then through caustic potash to a gas-holder.

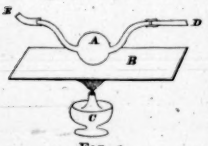


FIG. 5.

As mentioned before, a glass combustion tube may be used, in which case, of course, it should be straight, with stoppers fitting at each end. When glass is employed, a little more time is necessarily required, owing to the caution which must be used in heating and cooling.

I do not deem it necessary to speak of the advantages of the platinum over the glass tube, but I will simply say that its cost is soon paid for in time and labor saved.

I prefer manganese oxide to copper oxide, even if the old method of combustion is employed, because it is much lighter, quite as effective, and forms a mass more easily permeable by the gases.

ON THE OCCURRENCE OF SOLID HYDROCARBONS IN PLANTS.

By Helen C. De S. Abbott and Henry Trimble.

When many plants of the higher botanical orders are exhausted with petroleum-ether, crystalline compounds may be separated from the extracts which have not been previously noticed. The compounds are also obtained when alcohol or ether is used as a solvent; but it is preferable, on account of the greater number of constituents extracted by these menstrua, to employ petroleum-ether, and thus avoid certain difficulties of separation. Among the plants in which to this time these compounds have been discovered, may be mentioned *Cascara amarga*, *Phlox Carolina* and the *Phlox* species, and in other species of three or four natural orders.

The crystals from these petroleum-ether extracts were first noticed in 1884 and were announced in 1886 as a "camphor-like body."

Subsequent investigations proved this body to be a mixture; and by extracting 25 and 20 kilos of *Cascara amarga* and *Phlox Carolina* respectively, a satisfactory quantity was obtained. The method adopted to purify was, after removal of fats and coloring matter, to crystallise from boiling absolute alcohol. By fractional crystallisation at least three different compounds have been separated. One only of these has been studied. It melted at 196.2° C. to 196.4° C.; at higher temperatures it was decomposed, with an odor like sandal wood. It was soluble in petroleum-ether, ethylic and acetic ethers, benzol, chloroform, hot alcohol, glacial acetic acid, acetic anhydride, and linseed oil. From most of these solvents it readily separated in silky acicular crystals, often two to four centimeters in length.

The first ultimate analysis of this purified product from *Cascara amarga* gave the following results:

	I.	II.	III.
C	86.30	86.29	86.33
H	12.96	12.96	12.83
	99.26	99.25	99.16

These figures pointed strongly to the conclusion that the compound was a solid hydrocarbon. Liquid hydrocarbons are abundant in the plant kingdom, but a similar occurrence of this class of compounds in a solid or crystalline condition appears not to have been noticed.

By further purification of an additional quantity of the mixture the following results were obtained:

I. 0.1058 gram gave 0.3413 CO_2 and 0.1133 H_2O.

II. 0.1113 gram gave 0.3588 CO_2 and 0.1193 H_2O.

	I.	II.
C	87.97	87.89
H	11.89	11.90
	99.86	99.79

Fifteen kilos of *Phlox Carolina* were exhausted, the compound separated and repeatedly crystallised. Its ultimate analysis gave the following:

I. 0.1117 gram gave 0.3600 CO_2 and 0.1208 H_2O.

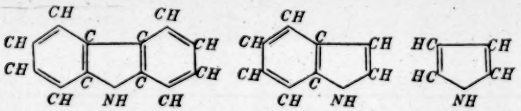
II. 0.1314 gram gave 0.4228 CO_2 and 0.1421 H_2O.

	I.	II.	Theory for $(C_{11}H_{18})_n$.
C	87.90	87.76	88.00
H	12.02	12.02	12.00
	99.92	99.78	100.00

ON THE RELATIONS EXISTING BETWEEN CARBAZOL AND PYRROL.

By Samuel C. Hooker.

The theoretical relation existing between carbazol, indol, and pyrrol is well shown by comparing their formulæ as follows:



Carbazol. Pyrrol. Indol.

The analogy existing between indol and pyrrol has received important experimental demonstration from the researches of v. Baeyer, E. Fischer,[1] and Ciamician,[2] but up to the present time no material evidence has been accumulated to show that a similar relation exists between carbazol and pyrrol. The formation of carbazol from thiodiphenylamine[3] by the action of copper furnishes some proof in support of the formula given above; but as this is the only reaction clearly tending to show that carbazol is a di-ortho derivative of diphenyl, and therefore that it contains the pyrrol ring, further evidence in the same direction appears desirable.

In making the experiments which led up to the facts here recorded, I hoped to find points of resemblance between carbazol and pyrrol for which the >NH group alone, independent of the pyrrol ring, would not account, and thus to confirm indirectly the above formula of carbazol.

Runge, the discoverer of pyrrol, observed that its vapor in contact with pine moistened with hydrochloric acid, colored the wood intensely red. Von Baeyer subsequently described this reaction as being very characteristic of indol. It is interesting, therefore, to find that carbazol reacts similarly, though not so readily. In order to observe the reaction, soak the wood—an ordinary match-stem answers admirably—for a second or two in a hot alcoholic or acetic acid solution of carbazol, and then thrust it into the neck of a bottle containing concentrated hydrochloric acid, so as thoroughly to expose it to the action of the gas without bringing it in contact with the acid solution. The red color soon develops, and slowly increases in intensity. The shade is precisely similar to that produced by pyrrol.

Since carbazol may be regarded as a derivative of indol in which the two carbon atoms of the indol ring are connected with the group C_4H_4'', this observation appears directly to contradict one of the deductions made by Emil Fischer[4] in the course of his study of indol derivatives. "The fir-wood reaction," he says, "no longer occurs when both the carbon atoms of the indol ring are connected with alkyls."

It seemed necessary, therefore, to confirm my results by substituting synthetical carbazol for that extracted from coal tar, with which I first obtained the reaction. In spite of careful purification,

[1] Ber. d. chem. Ges. **19**, 2988. [2] Ibid. **19**, 3028. [3] Ibid. **20**, 232. [4] Ibid. **19**, 1570.

it is conceivable that the coal-tar carbazol might still retain traces of foreign substances capable of imparting to it the power of coloring the wood.

Through the kindness of Dr. A. Goske in forwarding to me a sample of carbazol recently obtained by him[1] by the action of copper on thio-diphenylamine, I have been able to confirm the results of previous experiments in a satisfactory manner.

It seems possible therefore that the di-alkyl derivatives of indol which do not, according to Emil Fischer, give the fir-wood reaction when the test is made in the usual way, may do so if the conditions of the experiment are somewhat varied.

Carbazol and Isatin.

The behavior of thiophene (and furfuran) in forming coloring matters with isatin and ortho-diketones, apparently similar to those of pyrrol, makes it probable that in such reactions the >NH group of pyrrol takes no part. Consequently, in the case of carbazol, as all the hydrogen atoms of the pyrrol ring, excepting that of the imide group, are already substituted, it is not to be expected that any similar coloring matters can be formed. For this reason I was surprised to find that the behavior of carbazol and isatin in the presence of sulphuric acid is such as to strongly suggest the indophenine reaction.

On adding concentrated sulphuric acid to carbazol and isatin, an intense blue color is developed as the substances dissolve. The reaction is extremely characteristic and can be used as a delicate test for the recognition of carbazol. The blue color of the solution does not appear to be affected by slightly warming, and even after standing some hours its intensity had not materially diminished or its color otherwise changed. Water precipitates an indigo-blue substance which very rapidly becomes lighter in color. In order to avoid this change, attempts were made to extract the blue coloring matter from the acid solution without the addition of water, by agitation with various solvents. These experiments proved unsuccessful, and the further study of the compound was abandoned.

Although the above is very like the indophenine reaction and its apparently analogous reaction in the case of pyrrol, I am inclined to believe, for considerations already mentioned, that the similarity

[1] Ber. d. chem. Ges. **20**, 232.

is apparent only and not real. Diphenylamine gives no reaction with isatin under the same circumstances.

Since diphenylene-oxide and diphenylene-sulphide are probably related to furfuran and thiophene, respectively, in the same way as carbazol is to pyrrol, it seemed of importance to ascertain whether these substances also behaved similarly with isatin. I was unable to obtain any reaction with diphenylene-oxide, and consequently it is probable that diphenylene-sulphide also will be found indifferent.

Carbazol and Quinone.

The compounds produced from pyrrol and benzoquinone have no corresponding members in the thiophene series, and would appear to be directly or indirectly dependent upon the >NH group for their existence; it therefore seemed possible that carbazol and benzoquinone might react with the formation of similar compounds.

If a small quantity of sulphuric acid, diluted with one or two volumes of acetic acid, is added drop by drop to an acetic acid solution of carbazol and benzoquinone, an intense carmine red solution is produced which passes into a reddish violet as the quantity of sulphuric acid is increased. Water precipitates from this solution a substance of the same color, which dissolves very readily in ether, chloroform, and alcohol.

On the addition of crystals of quinone to carbazol dissolved in concentrated sulphuric acid, an intense green color is imparted to the solution. Hence, according to the strength of the acid used, a reddish-violet or a green solution is obtained.

Similarly Victor Meyer and O. Stadler[1] have shown that benzoquinone reacts with pyrrol in two distinct ways. If aqueous solutions of the two are mixed, a violet coloring matter is produced, whereas in the presence of dilute sulphuric acid a green precipitate is formed. For purposes of comparison I repeated V. Meyer and Stadler's experiments. The violet coloring matter obtained dissolved in ether to a solution very similar in shade to that of the ethereal solution of the coloring matter from carbazol.

Before concluding that the formation of these compounds is in any way connected with the existence of the pyrrol ring, it seemed necessary to study the action of diphenylamine under similar

[1] Ber. d. chem. Ges. **17**, 1035.

circumstances. Sulphuric acid added to diphenylamine and quinone dissolved in acetic acid immediately colors the solution blue; on adding water, a violet substance is precipitated.

These reactions recall the coloring matters obtained by P. Greiff[1] by heating chloranil or quinone with methyldiphenylamine and other amines with or without the addition of zinc chloride. The similarity existing between the method of formation and the shade of Greiff's coloring matters and the violet compounds obtained as above described from pyrrol, carbazol and diphenylamine, renders it extremely probable that in both cases the coloring matters are perfectly analogous, and that their formation in the case of pyrrol and carbazol depends upon the amine character of these substances, and not upon the presence of the pyrrol ring. This view, which could not, unfortunately, be substantiated by analysis, owing to the great instability of the pyrrol compound, receives support from the fact already alluded to that thiophene gives no coloring matters with benzoquinone.

With reference to the green solution formed on adding quinone to carbazol dissolved in sulphuric acid, it seems probable that in this case quinone plays the part of an oxidising agent only, for the same green-colored solution is produced, as is well known, by the addition of oxidising agents generally under similar circumstances. It occurred to me therefore as not unlikely that quinone acts merely as an oxidising agent also, when in contact with pyrrol in acid solution, especially as V. Meyer and Stadler extracted hydroquinone in considerable quantities from the mother-liquor after the green compound had been filtered off. Confirmation of this view was obtained by reference to Anderson's[2] description of the properties of pyrrol. He states that ferric chloride causes a dilute hydrochloric acid solution of pyrrol to turn first *green* and then black. He adds that platinic chloride and potassic bichromate produce a black precipitate with the same solution.

A few experiments soon proved that not only ferric chloride, but potassic chromate or bichromate, platinic chloride, potassic ferricyanide, and even potassic nitrite under certain circumstances, all give, when added in small quantity to a dilute sulphuric acid solution of pyrrol, a green substance which passes more or less rapidly, according to the oxidising agent used and the acidity and degrees of concentration of the solutions employed, into the black

[1] Ber. d. chem. Ges. **12**, 1610. [2] Ann. Chem. (Liebig), **105**, 354.

compound observed by Anderson. With tolerably concentrated solutions of the oxidising agents, the transition is so rapid that the green color can be scarcely observed, even when the sharpest lookout for it is maintained throughout the experiment.

With a dilute solution of potassic chromate, the formation of the green substance may be readily seen, and the reaction compared with that of quinone. As it is not easy, however, to obtain the reaction at its best without a number of trials, I prefer to give the exact strength of the solutions which I found to give good results. Eight drops of pyrrol are dissolved in 10 cc. of water to which eight drops of sulphuric acid have been added. When this is mixed with an 0.1 per cent. solution of potassic chromate in equal volumes, the green color is almost immediately developed, and rapidly increases in intensity until the solution becomes perfectly opaque. At this stage three or four volumes of water are added. The diluted solution is green in color, and slowly deposits a dark green or black precipitate.

A very dilute aqueous solution of quinone behaves almost precisely similarly with the above solution of pyrrol, but the precipitate formed is at first much greener than when potassic chromate is the oxidising agent used. It gradually darkens, however, and after some hours becomes almost black. If the green precipitate from quinone is washed with an 0.05 per cent. solution of potassic chromate, it is very rapidly blackened.

From these experiments it would appear extremely probable, therefore, that quinone does not condense with pyrrol in acid solution, but merely acts like other oxidising agents.

The formation of green substances like the above is not confined to the action of oxidising agents on carbazol and pyrrol. It has long been known that nitrous acid and other oxidising agents added in small quantity to diphenylamine dissolved in sulphuric acid, produce an intense blue solution from which water precipitates a green compound; this, like the corresponding compounds from carbazol and pyrrol, is insoluble in ether.

Pyrrol and Picric Acid.

The behavior of indol and carbazol in combining with picric acid suggested the idea that probably pyrrol would form a similar compound. On adding picric acid to an excess of pyrrol, a red color is at once developed; on warming, the picric acid is dissolved, and

the solution, when cold, deposits beautiful red needles. Similarly, if picric acid and an excess of pyrrol are dissolved in alcohol, long red needles, half or three quarters of an inch in length, can be readily obtained as the solution is allowed to evaporate. The compound is very unstable, and commences to decompose in the air as soon as the crystals are dry. Its fusing point is about 71°. Since the basic properties of pyrrol are very weak, and no well defined salts have been obtained with acids generally, the above described compound must be considered as analogous to the picric acid compounds of the hydrocarbons. The relation of pyrrol to benzol, so often dwelt upon by Victor Meyer, is thus once again emphasised. Phenyl-pyrrol also forms an unstable compound with picric acid. The compounds of pyrrol and its derivatives with picric acid will be further studied, and an attempt will be made to analyse them.

LABORATORY OF THE FRANKLIN SUGAR REFINERY, PHILADELPHIA, *June* 17, 1888.

ON THE ACTION OF ETHYLENE BROMIDE ON THE SODIUM DERIVATIVES OF THE ETHERS OF ACETO-ACETIC, BENZOYL-ACETIC AND ACETONE-DICARBOXYLIC ACIDS.

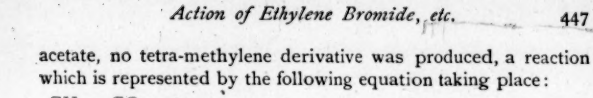
BY P. C. FREER AND W. H. PERKIN, JR.[1]

The remarkable difference in the behavior towards tri-methylene bromide of the sodium derivative of malonic ether as compared with those of aceto-acetic, benzoyl-acetic, and acetone-dicarboxylic acids has previously been shown by one of us.[2] In the case of malonic ether, a tetra-methylene derivative, the so-called tetra-methylene-dicarboxylic ether, $(COOC_2H_5)_2\,C\!\begin{array}{l}-CH_2\\ |\quad |\\ CH_2-CH_2\end{array}$ was formed; whereas, for example, by substituting ethylic sod-aceto-

[1] Abstract of a paper which appeared in the Journal of the Chemical Society (London), Vol. 51, p. 820. Communicated by the authors.

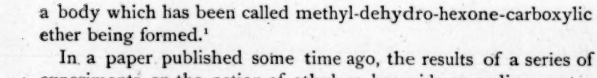
[2] W. H. Perkins, Jr., J. Chem. Soc. **51**, 702.

acetate, no tetra-methylene derivative was produced, a reaction which is represented by the following equation taking place:

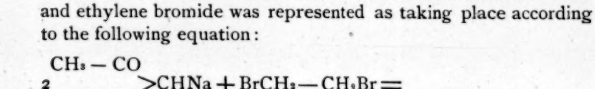


a body which has been called methyl-dehydro-hexone-carboxylic ether being formed.[1]

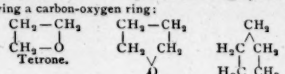
In a paper published some time ago, the results of a series of experiments on the action of ethylene bromide on sodium aceto-acetic and sodium benzoyl-acetic ethers were given. The substances formed in this reaction were assumed to be tri-methylene derivatives. Thus the reaction between sodium aceto-acetic ether and ethylene bromide was represented as taking place according to the following equation:



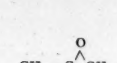
From the results of the experiments with tri-methylene bromide, mentioned above, it seemed, however, more probable that the above decomposition would be represented as follows:



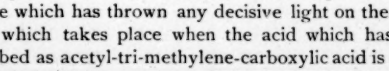
[1]After some discussion, we have decided upon the following system of nomenclature for this and similar bodies having a carbon-oxygen ring:



Tetrone. Pentone. Hexone.

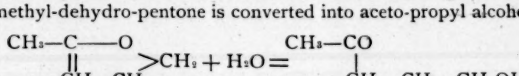
A body of the formula  is therefore methyl-dehydro-hexone-carboxylic ether.

in which case the product would be ethylic methyl-dehydro-pentone carboxylate. This possibility made it necessary to study the reaction again in the hope of being able to determine whether these compounds were pentone or tri-methylene derivatives. In experimenting with this end in view, a large number of reactions have been studied, the majority of which can be equally well explained on the assumption of either the tri-methylene or the pentone formula, the only one which has thrown any decisive light on the question being that which takes place when the acid which has already been described as acetyl-tri-methylene-carboxylic acid is distilled.[1] The acid is, during this operation, split into carbonic anhydride and a colorless oil which proved to be a mixture of two substances, the one which is present in by far the larger quantity being the substance which was previously (loc. cit. p. 710) described as acetyl-trimethylene, boiling at 113°; the other, and lesser in quantity, being an oil of ethereal odor, boiling at 90°. The constitutional formulæ of these two substances, the latter having proved to be the anhydride of aceto-propyl alcohol, are therefore:



Acetyl-tri-methylene, b. p. 113°. Methyl-dehydro-pentone, b. p. 93° (?).

The remarkable difference between these two compounds is seen in their behavior towards water at ordinary temperatures. Acetyl-tri-methylene does not dissolve, and remains unchanged, whereas methyl-dehydro-pentone is converted into aceto-propyl alcohol.



Methyl-dehydro-pentone. Aceto-propyl alcohol.

The latter is soluble in water.

The further examination of acetyl-tri-methylene has shown that it is a methyl-ketone, and a saturated body, so that the only formula which can be assigned to it, at all events according to our present knowledge of chemical structure, is the one given above.

The constitution of ethylic acetyl-tri-methylene carboxylate, as deduced from the above experiments, is very remarkably supported by the study of its magnetic rotation, as well as that of its

[1] J. Chem. Soc. **47**, 702.

decomposition products, which has been undertaken by W. H. Perkin, Sr. The only constitutional formula possible for ethylic acetyl-tri-methylene carboxylate other than that given above, is that of ethylic vinyl-aceto-acetate, $\begin{matrix} CH_3—CO \\ | \\ COOC_2H_5CH—CH:CH_2 \end{matrix}$. This, however, differs from allyl-aceto-acetic ether in having one CH_2 group less than the latter. It therefore follows that the magnetic rotation of vinyl-aceto-acetic ether should be that of allyl-aceto-acetic ether (10.383) less the value of one CH_2 group (1.023), that is, it should be 9.360. Now, the magnetic rotation of the purest sample of acetyl-tri-methylene-carboxylic ether as yet examined is 8.198, a number which shows that it cannot be vinyl-aceto-acetic ether.

Against the conclusions deduced from the results of the chemical examination of the products of distillation of acetyl-tri-methylene-carboxylic acid it might be urged that during this reaction some intra-molecular change had taken place. The following considerations will show that this is not the case. The magnetic rotation of acetyl-tri-methylene is 5.245. If acetyl-tri-methylene is really the basis of the original product of the action of ethylene bromide on sodium aceto-acetic ether, it follows that the magnetic rotation of this substance should differ from that of acetyl-tri-methylene-carboxylic acid by the value of the group ($COOC_2H_5—H$). This number is easily obtained by subtracting the magnetic rotation of acetone from that of aceto-acetic ether, and is thus found to be 2.987. If we now add this to the magnetic rotation of acetyl-tri-methylene we obtain the number 8.232 as the calculated magnetic rotation of acetyl-tri-methylene-carboxylic ether. This agrees closely with that actually found (8.198), so that at present both the chemical reactions and the physical measurements are in favor of the assumption that these compounds are tri-methylene derivatives.[1]

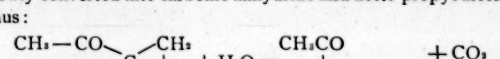
Of the samples used in determining the physical properties of acetyl-tri-methylene-carboxylic ether, some were prepared by careful fractioning of the raw product of the action of ethylene bromide on sodium aceto-acetic ether, while others were made by the action of ethyl iodide on the silver salt of acetyl-tri-methylene-carboxylic acid. The ether, as prepared by the latter method, is a colorless

[1] For a complete list of the numbers obtained as the magnetic molecular rotation of acid and alcohol ethers of the fatty series, as well as the methods employed in their determination, see W. H. Perkin, J. Chem. Soc. **45**, 421.

oil, boiling between 195.6 and 196.6, and giving as its magnetic molecular rotation the number 8.198.

In order to prepare acetyl-tri-methylene-carboxylic acid from its ethereal salt, the fraction of the crude product of the action of ethylene bromide on the sodium derivative of aceto-acetic ether, boiling between 180° and 200°, is mixed with twice the calculated quantity of caustic potash dissolved in methyl alcohol, and the whole then boiled for five hours on a water-bath. The alcohol is distilled off, the product dissolved in water, and the solution then evaporated in an open basin until the last traces of alcohol have disappeared; when cool, dilute sulphuric acid is added in excess, and the whole is then extracted about ten times with pure ether. The solution, upon evaporating, deposits the acid in the form of a slightly brownish oil.

Acetyl-tri-methylene-carboxylic acid, when boiled with water, is slowly converted into carbonic anhydride and aceto-propyl alcohol, thus:



This reaction is complete at the expiration of fourteen hours, a clear solution resulting. Aceto-propyl alcohol is isolated from this by saturation with anhydrous potassic carbonate and repeated extraction with pure ether. After evaporating the ether, a colorless oil remains which cannot be purified by distillation at ordinary pressures, as it is decomposed, to some extent, into its anhydride and water. When rapidly fractioned under a pressure of 100 mm. it is obtained, nearly free from anhydride, as a colorless oil, boiling between 144° and 145°. Its magnetic rotation is 5.544; that of aceto-butyl alcohol, $CH_3.CO.CH_2.CH_2.CH_2.CH_2OH$, is 6.502; the difference between these two numbers being 0.958, a number closely agreeing with that of the true numerical value of the CH_2 group, viz. 1.023. This clearly shows that aceto-propyl alcohol and aceto-butyl alcohol must belong to a homologous series. The slight deviation is caused by the impossibility of obtaining aceto-propyl alcohol free from its anhydride. The constitution of aceto-butyl alcohol has been proved by the formation of acetic and succinic acids upon the oxidation of that substance with chromic acid. Aceto-propyl alcohol is a colorless syrup, mixing with water in all proportions. When slowly heated it is completely

decomposed into its anhydride and water, the distillate consisting of two layers which, however, form a homogeneous mixture after standing for some hours. The phenyl-hydrazine compound could not be obtained in a crystalline state.

As has been previously stated, acetyl-tri-methylene-carboxylic acid is decomposed, on distillation, into acetyl-tri-methylene and a volatile oil, boiling at 93°. This is identical with the anhydride of aceto-propyl alcohol. The difference between acetyl-tri-methylene and this anhydride has already been mentioned.

Ethylic acetyl-tri-methylene carboxylate combines readily with hydrogen bromide, ethylic ω-brom-ethyl aceto-acetate being formed, thus:

$$CH_3-CO \quad CH_2 \qquad\qquad CH_3CO$$
$$COOC_2H_5 > C < | + HBr = H > C - CH_2 - CH_2Br.$$
$$CH_2 \qquad\qquad COOC_2H_5$$

This is a heavy oil, of slightly yellowish color which changes to brown when the substance is exposed to the air, hydrogen bromide being at the same time evolved. The oil cannot be distilled. When treated with zinc dust and acetic acid, ethyl-aceto-acetic ether is produced. When boiled with dilute hydrochloric acid for about two hours, ethylic ω-brom-ethyl aceto-acetate is completely dissolved, carbon dioxide, alcohol, and aceto-propyl alcohol being produced. This latter was found to be identical with the alcohol as obtained by boiling acetyl-tri-methylene-carboxylic acid with water.

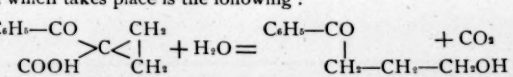
If aceto-propyl alcohol be dissolved in about five parts of water, and to this solution the theoretical quantity of three per cent. sodium amalgam be slowly added, reduction, without evolution of gas, sets in immediately. The product of this reaction is isolated by saturating the liquid with anhydrous potassic carbonate and extracting repeatedly with pure ether. By this means a colorless oil, boiling between 210° and 220°, with slight decomposition when rapidly distilled, is obtained. This substance is γ-pentylene-glycole,

$$CH_3.CH.CH_2.CH_2.CH_3$$
$$OH \qquad\qquad OH.$$

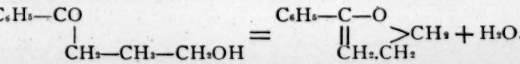
When this substance is heated on a water-bath with fifty per cent. sulphuric acid, it is decomposed into its anhydride and water. The latter is a volatile oil of ethereal odor, boiling between 78° and 83°. The formula of this substance is as follows:

$$CH_3-CH.CH_2-CH_2-CH_2-O$$
$$\text{└}_____\text{┘}$$

After the results obtained in studying the action of water on acetyl-tri-methylene-carboxylic acid, when, as has previously been stated, decomposition into carbonic anhydride and aceto-propyl alcohol takes place, it was thought that it would be interesting to experiment on the behavior of benzoyl-tri-methylene-carboxylic acid under similar conditions. One gram of the acid, in as finely divided a state as possible, was heated in a sealed tube with 40 cc. of water for four or five hours at 100°–110°, the tube being frequently taken out and well shaken. On opening the tube, the contents were found to consist of an almost perfectly clear liquid. In order to separate the few oily drops swimming about, the whole was filtered through a wet filter, and the product of the reaction separated from the now perfectly clear filtrate by saturation with anhydrous potassium carbonate and repeated extraction with ether. This ethereal solution, after drying, filtering, and evaporating, deposited a colorless oil of aromatic odor, which the analysis showed was not benzoyl-propyl alchohol, but the anhydride of that body. In this decomposition it is evident that the first reaction which takes place is the following:



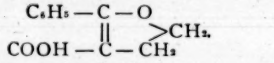
That a ketone alcohol is present in the aqueous solution can be proved by the addition of phenyl-hydrazine acetate, when an oily phenyl-hydrazine compound is at once precipitated. However, upon extracting with ether and drying over anhydrous potassic carbonate, this unstable ketone alcohol is at once converted into its anhydride and water:



The instability of these aromatic ketone alcohols is very remarkable. Aceto-butyl alcohol, when rapidly heated, can be distilled almost without change, whereas the corresponding aromatic alcohol, benzoyl-butyl alcohol, is split into its anhydride and water on simply standing over sulphuric acid for a few days. Aceto-propyl alcohol, although not so stable as aceto-butyl alcohol, can be distilled unchanged under a pressure of 100 mm., whereas benzoyl-propyl alcohol only exists in aqueous solution, and on isolation

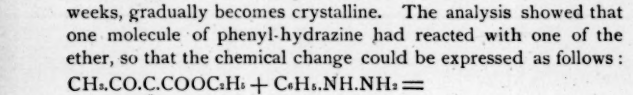
is at once converted into its anhydride. It still remains to be determined whether the anhydride of benzoyl-propyl alcohol is identical with the body previously described as benzoyl-tri-methylene.[1]

It seems almost probable that if these anhydride rings are so easily formed in the aromatic series, the derivatives obtained from benzoyl-acetic ether and ethylene bromide are to be classified as pentone and not tri-methylene substances, in which case the acid described as benzoyl-tri-methylene-carboxylic acid would have the formula,

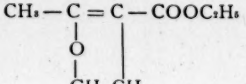


Further experiment must decide this point.

In order to prove the presence of a carbonyl group in acetyl-tri-methylene-carboxylic ether, several experiments on the action of phenyl-hydrazine on this substance were made. If the ether be mixed with a little less than the theoretical quantity of phenyl-hydrazine, the mixture then heated on a water-bath until all reaction has ceased, and the whole then submitted to distillation in steam, in order to drive off any unchanged ether, a heavy, brownish oil remains behind. This product, when allowed to stand for six weeks, gradually becomes crystalline. The analysis showed that one molecule of phenyl-hydrazine had reacted with one of the ether, so that the chemical change could be expressed as follows:



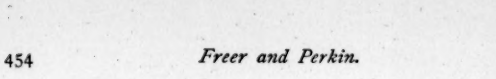
This would appear to be an additional proof that acetyl-tri-methylene-carboxylic ether is really a tri-methylene derivative, and does not contain an oxygen-carbon chain, as it would were its formula as follows:



During the course of these experiments it appeared interesting

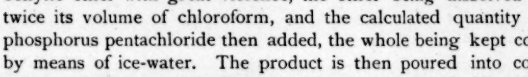
[1] J. Chem. Soc. **47**, 840.

to try the action of oxidising agents on acetyl-tri-methylene-carboxylic acid, or its ethereal salt, in the hope that in this way trimethylene-di-carboxylic acid (1.1) might be produced, thus:

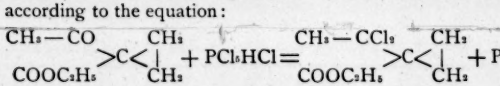


The experiments, both in acid solution with chromic acid, and in alkaline solution with potassic permanganate, as well as with iodine, gave negative results. As the chief products of oxidation, oxalic and acetic acids were observed, while in the case of iodine, iodoform was produced.

Phosphorus pentachloride reacts with acetyl-tri-methylene-carboxylic ether with great violence, the ether being dissolved in twice its volume of chloroform, and the calculated quantity of phosphorus pentachloride then added, the whole being kept cool by means of ice-water. The product is then poured into cold water, and the heavy oil which separates extracted with ether. By this means a heavy fluid is obtained, upon evaporation of the ether, the boiling point being between 171°–173°, 150 mm. On each fractioning it was noticed that traces of hydrogen chloride were given off, so that, even under a pressure of 35 mm., some decomposition takes place upon boiling. This chlorinated compound is a colorless oil of powerful odor which, upon standing, soon becomes yellow. The analysis proved that it contained two chlorine atoms to the molecule. Its constitution can be expressed by either of the two following formulæ:



of which the second seems the more plausible. The most probable explanation of the action of phosphorous pentachloride on acetyl-tri-methylene-carboxylic ether is as follows: A substance, the constitution of which is represented by formula I, is first formed according to the equation:



This substance is further acted upon by the hydrochloric acid which is always present; the tri-methylene ring is split, and a change takes place which can be represented by the following equation:

$$\begin{matrix}CH_3-CCl_2\\ COOC_2H_5\end{matrix}\!\!>\!C\!<\!\begin{matrix}CH_2\\ |\\ CH_2\end{matrix} + HCl = \begin{matrix}CH_3-CCl_2\\ COOC_2H_5\end{matrix}\!\!>\!CH-CH_2-CH_2Cl.$$

This intermediate compound then loses one molecule of hydrochloric acid, probably during the reaction, possibly upon distillation, when a substance results, the constitution of which is represented by formula II:

$$\begin{matrix}CH_3-CCl_2\\ COOC_2H_5\end{matrix}\!\!>\!CH-CH_2-CH_2Cl = \begin{matrix}CH_3-CCl\\ COOC_2H_5\end{matrix}\!\!>\!C-CH_2-CH_2Cl + HCl.$$

The hydrochloric acid thus produced could react with a fresh quantity of the original compound, and thus a continuous reaction be set up. The behavior of this substance, which may be called ethylic chloro-ethyl-chloro-crotonate, toward reducing agents has tended to confirm the above speculations. By reduction with zinc dust and hydrochloric acid in alcoholic solution, an oil consisting of an acid and a neutral substance is obtained. These are separated by means of sodic carbonate, from which the acid is obtained as a crystalline solid when the solution is acidified. This crystalline body was found to correspond to chloro-ethyl-crotonic acid obtained by Demarcais by treating ethyl-aceto-acetic ether with phosphorus pentachloride. The formation of chloro-ethyl-crotonic acid from chloro-ethyl-chloro-crotonic ether can be explained according to the following formula:

$$\begin{matrix}CH_3-CCl\\ \quad\diagdown\!\!\diagup C\\ COOC_2H_5\end{matrix}\!\!-CH_2-CH_2Cl + H_2 = \begin{matrix}CH_3-CCl\\ \quad\diagdown\!\!\diagup C\\ COOH\end{matrix}\!\!-CH_2-CH_3 + C_2H_5Cl.$$

We intend repeating these experiments with larger quantities of substance. The neutral oil which was mentioned above has not been further examined.

By means of reduction of chloro-ethyl-chloro-crotonic ether with either sodium amalgam or hydriodic acid and phosphorus, di-ethyl-acetic acid was obtained, as follows:

$$\begin{matrix} CH_3CCl \\ COOC_2H_5 \end{matrix}\!\!>\!C-CH_3-CH_2Cl+3H_2+H_2O=$$

$$\begin{matrix} CH_3CH_2 \\ \quad\quad HC \\ COOH \end{matrix}\!\!>\!CH-CH_3+C_2H_5OH+2HCl.$$

The action of ethylene bromide on acetone-dicarboxylic ether have some interesting results. In studying this reaction, a mixture of 40 grams of ethylic acetone-dicarboxylate and 38 grams of ethylene bromide was slowly added to a well cooled solution of 9 grams of sodium dissolved in 100 grams of alcohol and the whole boiled on a water-bath for ten hours. In order to isolate the principal product of the reaction, the excess of alcohol was distilled off, the residue mixed with water, and the whole extracted with ether. The yellowish oil which remained after evaporation of the ether was submitted to fractional distillation. It was found to consist for the most part of unchanged acetone-dicarboxylic ether and a colorless oil, boiling between 223° and 224° (150 mm.). The analyses of the latter agreed with the formula of ethylic acetyl-tri-methylene-dicarboxylate. This substance is quite unstable, a fact which accounts for the small yield, which was but ten per cent. Besides the oil boiling between 223° and 224°, another, boiling at 130°–200° (150 mm.), was separated. This latter, when refractioned at ordinary pressures, proved to be acetyl-tri-methylene-carboxylic ether.

Ethylic acetyl-tri-methylene carboxylate is produced from ethylic acetyl-tri-methylene dicarboxylate by partial hydrolysis and subsequent splitting off of carbon dioxide, thus:

$$COOC_2H_5-CH_2-CO \quad \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} + H_2O=$$

$$\begin{matrix} COOC_2H_5 \end{matrix}$$

$$COOH-CH_2-CO \quad \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} = COOC_2H_5\,CH_2-CO \quad \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>\!C\!<\!\!\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} + CO_2.$$

Acetyl-tri-methylene-dicarboxylic acid can only be prepared from its ethereal salt by saponification in the cold, twice the calculated quantity of pure potash dissolved in methyl alcohol being used. The reaction is complete at the expiration of twelve days. The

product is diluted with water, acidified with sulphuric acid, and extracted with ether. The crystalline acid is spread on a porous plate and washed with cold chloroform. Thus purified it is a white solid, melting with decomposition at about 175°. Upon boiling with water it is split into aceto-propyl alcohol and two molecules of carbonic anhydride, just as acetyl-tri-methylene-monocarboxylic acid was decomposed into aceto-propyl alcohol and one molecule of carbon dioxide. When acetyl-tri-methylene-dicarboxylic acid is heated above its melting point, carbon dioxide is evolved and acetyl-tri-methylene formed.

These experiments with acetone-dicarboxylic ether were performed in the hope of obtaining a penta-methylene derivative, thus:

$$\begin{array}{l} COOC_2H_5-CHNa \quad BrCH_2 \\ \qquad\quad | \qquad\quad | \\ \qquad\quad CO \quad + \quad | \quad = \\ \qquad\quad | \qquad\quad | \\ COOC_2H_5-CHNa \quad BrCH_2 \end{array}$$

$$\begin{array}{l} COOC_2H_5-CH-CH_2 \\ \qquad\quad | \qquad\quad | \\ \qquad\quad CO \quad | \quad + 2NaBr. \\ \qquad\quad | \qquad\quad | \\ COOC_2H_5-CH-CH_2 \end{array}$$

The result has shown that no such body is produced, the ether of acetyl-tri-methylene-dicarboxylic acid,

$$COOC_2H_5-CH_2-CO \quad CH_2 \quad ,$$
$$\qquad\qquad\qquad\quad >C< \quad |$$
$$COOC_2H_5 \qquad\quad CH_2$$

being formed.

Some of the reactions described in the foregoing, especially that of the decomposition of acetyl-tri-methylene-carboxylic acid upon boiling with water, are undoubtedly difficult to explain on the assumption that this substance, as well as the others mentioned, are really tri-methylene derivatives. At the same time it must be remembered that the properties of such a ring as that present in tri-methylene derivatives are at present wholly unknown, and that therefore no definite argument against their acceptance as such bodies can be based upon these peculiarities.

The foregoing research was conducted, in the beginning, in the laboratory of Prof. v. Baeyer, at Munich; later, at the kind invitation of Professor Dixon, we were enabled to continue it at the Owens College, Manchester, England.

BOSTON, MASS., *November*, 1887.

COEFFICIENTS OF VOLATILITY FOR AQUEOUS CHLORHYDRIC ACID.

By Robt. B. Warder.

Aqueous chlorhydric acid may be represented by the formula $H_2O + nHCl$, where n is the number of molecules of the acid divided by the number of molecules of water. On boiling, the residue usually approaches the constant composition $H_2O + \frac{1}{8}HCl$, as shown by Roscoe and Dittmar. If the composition of the distillate formed at any moment is represented as $H_2O + vnHCl$, the factor v expresses the coefficient of volatility.

Chlorhydric acid of convenient strength was distilled, the boiling flask being so heated that no moisture should condense on the sides, to vitiate the results by dephlegmation. The several fractions of distillate were weighed and titrated, and the varying composition of the boiling liquid was calculated from the weights of water and acid removed.

In one distillation, with rapid boiling, the values agree well with the formula $v = 445n^3$, as shown by the following numbers:

n.	vn.		v.	
	Observed.	Calculated.	Observed.	Calculated.
.0681	.0095	.0095	.140	.140
.0759	.0147	.0148	.194	.195
.0862	.0243	.0245	.282	.285
.0984	.0422	.0417	.429	.424
.1107	.0661	.0669	.597	.604

The results obtained under the conditions of the experiments agree with the following statements, which must not be pressed too closely for other conditions:

I. When dilute acid ($n = .07$ to $.11$) was boiled rapidly, v was found to be equal to $445n^3$.

II. When dilute acid was boiled more slowly, the values of v were diminished about 10 to 30 per cent.

III. When strong acid ($n = .15$ to $.20$) was boiled rapidly, the values of v were greater than those indicated by the formula given above, being approximately represented by the equation $v = 3063n^4$.

Fuller details may be expected later.

Washington, D. C., *July*, 1888.

THE ACTION OF SULPHURETTED HYDROGEN ON ARSENIC ACID.

(SULPHOXYARSENIC ACID.)

BY LEROY W. MCCAY.

Introduction.

According to Wackenroder,[1] Ludwig[2] and H. Rose,[3] sulphuretted hydrogen first reduces arsenic acid to arsenious acid, with the separation of sulphur, and then precipitates the arsenic as the trisulphide. The reaction is said to take place in two distinct phases:

(1). $As_2O_5 + 2H_2S = As_2O_3 + 2H_2O + 2S$, and

(2). $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$.

Fuchs[4] investigated the subject in 1862, and concluded that Rose and his predecessors were right. In 1878, Bunsen[5] proved that they were all wrong. He showed that when certain conditions were fulfilled, the arsenic present in an acidified solution of an arseniate could be directly and completely precipitated by sulphuretted hydrogen as the pentasulphide. Lately having had occasion to go over Bunsen's work, I[6] discovered that the arsenic in an acidified solution of an alkali arseniate could be directly and completely precipitated by sulphuretted hydrogen as the pentasulphide, in one hour, by simply causing the sulphuretted hydrogen to act upon the arsenic acid under pressure and in the absence of air.

Fresenius[7] says that when a current of sulphuretted hydrogen, in excess, is passed into an acidulated solution of arsenic acid, kept at 70° C., the pentasulphide is formed. The precipitate obtained under other circumstances, however, is, according to him, a mixture of the pentasulphide, trisulphide, and sulphur. Brauner and Tomiček[8] have of late done considerable work upon the subject. They substantiate Fresenius' results. With a hot solution of arsenic acid and a rapid current of sulphuretted hydrogen they obtained the pentasulphide; with a hot solution of arsenic acid and a slow current of the gas, they obtained a mixture of the pentasulphide, the trisulphide, and sulphur. They use the ordinary equations to indicate the reactions which take place during

[1] Dictate of Forensic Chemistry.
[2] Archiv der Pharm., 2te Reihe, **97**, 32.
[3] Ann. der Phys. u. Chem. **107**, 186.
[4] Ztschr. anal. Chem. **1**, 189.
[5] Ann. Chem. (Liebig) **192**, 305.
[6] This Journal **9**, 174.
[7] Qualitative Analyse, 15te Auflage.
[8] Chem. Soc. (Feb. 1888), 145.

the formation of the mixture. Why, when the current of gas is rapid, the pentasulphide is alone formed, while, when the current is slow, the mixture of the pentasulphide, the trisulphide, and sulphur results, they confess themselves unable to explain. They consider the problem as one belonging to the domain of chemical dynamics.

The object of this paper is to remove the mystery which is connected with the formation of the above-mentioned mixture of the pentasulphide, trisulphide, and sulphur. With the exception of that of Brauner and Tomiček, all the work which has thus far been undertaken with the view of explaining the irregularities connected with the action of sulphuretted hydrogen upon arsenic acid, has been of a qualitative nature. Bunsen's researches were essentially of an analytical character. In his paper upon the separation of antimony from arsenic with sulphuretted hydrogen, he did not endeavor theoretically to account for the fact that his precipitate, in determining the arsenic, was the pure pentasulphide and not the trisulphide and sulphur, or a mixture of the pentasulphide, the trisulphide, and sulphur.

The Reduction Hypothesis.

For some time past Rose's explanation has appeared to me inadequate. That it is partially false follows directly from the work of Bunsen, Fresenius, and Brauner and Tomiček. I believe that the experiments below described prove that reduction does not take place.

Having accidentally discovered that very small quantities of sulphuretted hydrogen produce, even after prolonged action, no precipitate of sulphide of arsenic in moderately concentrated solutions of alkali arseniates acidified with a mineral acid, I tried the following experiment:

25 cc. of a solution of potassium arseniate containing 25 grams of the salt in two liters of water were brought into a 200 cc. flask, and rendered faintly acid with sulphuric acid. 10 cc. of sulphuretted hydrogen water containing 0.0204 gram sulphuretted hydrogen were then added, and the whole was diluted with freshly boiled cold water to within about a centimeter of the mouth of the flask. The flask was then corked, well shaken, and allowed to stand in a cold place until all odor of sulphuretted hydrogen had disappeared, and a piece of paper moistened with acetate of lead and

held over the mouth of the flask gave no reaction for the gas. The flask and contents stood twelve hours.

At the end of this time a very slight opalescence appeared in the liquid, due to the separation of sulphur. In order to determine the weight of the sulphur, the contents of the flask were poured into a beaker containing some pure asbestus pulp, stirred thoroughly and filtered. The liquid passed through the filter perfectly clear. The pulp was thoroughly washed, dried over sulphuric acid, and then extracted with chemically pure carbon bisulphide. On evaporating the liquid, a slight residue of sulphur weighing 0.0005 gram was left. This corresponds to 0.00053 gram sulphuretted hydrogen.

The clear filtrate having been neutralised with sodium hydrate, mixed with sodium bicarbonate and a few drops of starch paste, was titrated with a $\frac{N}{10}$ solution of iodine. Instead of obtaining the elegant reaction so characteristic of Mohr's method for determining arsenious acid, I found it impossible to reach a point at which I could be sure that the reaction was complete. After 2–3 cc. of the iodine solution had been added, a bluish followed by a reddish color appeared, and this disappeared only after long and vigorous stirring. The phenomenon reminded me somewhat of the irregularities which, toward the end, invariably attend the titration with iodine of a solution of trisulphide of arsenic in sodium carbonate.[1] I have repeated this experiment several times, but the results have always been the same. It certainly disproves the reduction hypothesis; for if this hypothesis were true, the sulphur found, calculated to sulphuretted hydrogen, should have equalled 0.0204 gram, and the number of cubic centimeters of $\frac{N}{10}$ iodine used for titrating 10 cc. of the sulphuretted hydrogen water should have been equal to the number requisite for titrating the arsenious acid formed.

Sulphoxyarsenic Acid.

Since in all my experiments the quantity of sulphur formed proved so extremely small, it occurred to me that perhaps, by proper care, the separation of even traces might be prevented. Such, indeed, turned out to be the case. I found that by bringing 50 cc.

[1] Graeger. J. prakt. Chem. **96**, 261.

of the arseniate of potassium solution into a 500 cc. flask, acidifying with 5 cc. dilute sulphuric acid (1 : 10), adding 10 cc. sulphuretted hydrogen water, diluting to the mouth with freshly boiled cold water, corking, shaking well, and keeping for twelve hours in a dark place, and in a large vessel of ice-water, the solution lost all smell of sulphuretted hydrogen and yet remained absolutely clear.[1] The more dilute the solution and the lower the temperature, other things being equal, the less tendency there seems to be toward a separation of sulphur. It is possible then, under certain circumstances, for small quantities of sulphuretted hydrogen, in the presence of relatively large quantities of arsenic acid, completely to disappear as such without either precipitating arsenic as a sulphide or reducing arsenic acid to arsenious acid with the separation of sulphur. This point having been settled, I turned my attention to an examination of the liquid so obtained.

The first tests were performed upon a solution prepared precisely according to the details already given. Such a liquid, after the removal, if necessary, of the trace of sulphur with asbestus pulp, gave the following reactions: 1. When rendered strongly acid with sulphuric or hydrochloric acid, it remained for some time clear. 2. Mixed with sulphuretted hydrogen, it gave no precipitate.[2] Sometimes hours passed before a precipitate commenced to separate. 3. After boiling and shaking vigorously, it commenced to become opalescent; the opalescence gradually increased to a cloud, and before long, sulphur was deposited. During the reaction there was no sulphuretted hydrogen or sulphurous acid generated. 4. After the boiled liquid had cooled and the sulphur had been separated with asbestus, an addition of sulphuretted hydrogen produced an instantaneous precipitate of trisulphide of arsenic. 5. Sulphate of copper produced no precipitate. 6. Mercuric chloride gave a heavy yellowish white precipitate. 7. Nitrate of silver produced immediately a heavy black precipitate of sulphide of silver. The filtrate from this contained no arsenious acid, for, upon adding ammonia in excess, and a little more nitrate of silver, and boiling, there was no reduction to metallic silver.

[1] To 500 cc. water I added 0.25 cc. sulphuretted hydrogen water, and then a few drops of iodine solution. After standing about an hour, the liquid became distinctly opalescent. The 0.25 cc. sulphuretted hydrogen water = 0.0003 gram sulphuretted hydrogen.

[2] When there had been no separation of sulphur, the sulphuretted hydrogen produced absolutely no color. When sulphur had separated, the liquid, after the addition of the sulphuretted hydrogen, took on a faint yellow hue.

The liquid being clear, acid, and absolutely free from uncombined sulphuretted hydrogen, could contain no soluble sulphides, no sulpho-salts, and no hyposulphites. These compounds cannot exist, much less be formed, in the presence of strong mineral acids. Such being the case, it seemed possible that the compound which gives the above reactions might be one intermediate between arsenic and sulpharsenic acid, or sulphoxyarsenic acid.[1]

By passing a current of sulphuretted hydrogen slowly through a cold acidified solution of potassium arseniate until an opalescence appeared, removing the excess of gas with a few drops of sulphate of copper, and filtering, a liquid was obtained which gave all the above reactions. The reactions, however, were not as definite as could be desired. To render them so, I heated the solution of arsenic acid to about 70° C., treated it with a slow current of sulphuretted hydrogen until a yellow precipitate made its appearance, and then suddenly poured the whole upon crushed ice. After stirring well, decanting, and removing the free sulphuretted hydrogen by means of a few drops of sulphate of copper and filtering, I obtained a liquid which gave six[2] of the seven reactions with a degree of sharpness leaving nothing to be desired. I also prepared a liquid which showed all the reactions, by heating the solution of arsenic acid to about 70° C., treating it with a slow current of gas until an opalescence appeared, cooling it suddenly by pouring it upon crushed ice, and removing the uncombined sulphuretted hydrogen by means of a blast of air.

Potassium Sulphoxyarseniate.

In 1845, Bouquet and Cloez[3] announced the discovery of a new and highly interesting salt, which they prepared by treating a saturated solution of biarseniate of potassium with a rapid current of sulphuretted hydrogen. The salt was carefully analysed and proved to be biarseniate of potassium, in which, according to the dualistic view, two atoms of the oxygen in the arsenic acid were replaced by an equivalent quantity of sulphur. They called the salt sulphoxyarseniate of potash, and wrote the formula for it, $As_2O_3.S_2,K_2O + 2H_2O$. Owing to the ease with which the solutions of the salt split up into arsenite of potassium, water and

[1] See preliminary notice in the Chemical News **57**, 54.

[2] The presence of the sulphate of copper interferes with reaction No. 2.

[3] Ann. chim. phys., 3 Serie, **13**, 44.

sulphur, Bouquet and Cloez concluded that the corresponding acid could not exist in the free state. Since the paper of Bouquet and Cloez appeared, nothing has been published on the subject.[1] It appeared probable that the compound obtained by me might be the free sulphoxyarsenic acid.

In order to test this idea, the following experiments were made:

About half an ordinary test-tube full of a saturated solution of dihydrogen-potassium arseniate was treated for an hour with a rapid stream of sulphuretted hydrogen. The contents of the tube were then violently shaken for a few minutes, and permitted to stand until the precipitate formed had completely settled. Below the sulphide of arsenic there appeared a few colorless crystals. The mother-liquor, together with the sulphide of arsenic, were poured off as carefully as possible, the liquid immediately filtered, and, with it, the crystals were repeatedly washed until all yellow specks had been removed. The crystals were then washed with a very small quantity of pure water, pressed between filter paper, and dried over concentrated sulphuric acid in a vacuum. Only about 0.3 gram was obtained in this preliminary work, but the amount proved sufficient to substantiate my expectations and warrant further research.

To satisfy myself that I had to do with the pure salt, I made determinations of the arsenic and sulphur. The method of analysis in outline will be found further on.

Taken 0.2085 gram salt.

Calculated for H_2KAsO_2S.		Found.
As	38.26	38.67
S	16.35	16.24

The figures found agree with those calculated, in a most satisfactory way, and there can be no doubt about the purity of the salt.

The rest of the crystals were dissolved in about 100 cc. of water, and the solution made acid with dilute sulphuric acid: 1. the liquid remained absolutely clear for some time; 2. with sulphur-

[1] A. Geuther has described a sulphoxyarseniate of sodium, and K. Preis has lately prepared quite a number of what he calls oxysulpharseniates of sodium. These salts, however, were all obtained by acting on arsenious oxide with sulphide of sodium. Preis says that solutions of oxysulpharseniates of sodium, when boiled with excess of hydrochloric acid, give precipitates of pentasulphide of arsenic. Solutions of sulphoxyarsenic acid prepared as described in this paper give, when boiled with hydrochloric acid, a precipitate of sulphur. When the solutions are concentrated, this precipitate of sulphur is sometimes contaminated with traces of sulphide of arsenic. See A. Geuther, Ann. Chem. (Liebig) **240**, H. 2. Also K. Preis, Chem. Ztg. Repert. 1888, **23**, 73.

etted hydrogen it gave no precipitate; 3. when boiled, decomposition set in and sulphur was deposited; 4. the boiled liquid gave with sulphuretted hydrogen an instantaneous precipitate of yellow trisulphide of arsenic; 5. sulphate of copper occasioned no change; 6. mercuric chloride produced immediately a yellowish white precipitate; 7. nitrate of silver threw down a heavy black precipitate of sulphide of silver. These are the reactions which characterised the liquid obtained by first passing a slow current of sulphuretted hydrogen through an acidified solution of an alkali arseniate, and then removing all traces of the free gas by means of copper solution or a blast of air.

The fact that a dilute solution of sulphoxyarseniate of potassium in water can be rendered strongly acid with sulphuric or hydrochloric acid, without any separation of sulphur, proves conclusively that sulphoxyarsenic acid can exist in the free state, and the reactions given by such a dilute solution of the acid being identical with those given by the liquid prepared according to any one of the above mentioned methods, likewise prove conclusively that the body with which we have to do, and which is the cause of all the mystery and irregularity connected with the precipitation of arsenic from a solution of arsenic acid with sulphuretted hydrogen, is sulphoxyarsenic acid.

The filtered mother-liquor obtained in preparing the sulphoxyarseniate of potassium gave excellent reactions for sulphoxyarsenic acid. This fact showed that large quantities of the salt had failed to crystallise out. The concentrated liquor, however, decomposed very rapidly, arsenite of potassium, water, and sulphur being formed. I found that this tendency to decompose could be in a great measure retarded by simply diluting the liquid with large quantities of water and keeping it cold.

I prepared two samples of sulphoxyarseniate of potassium for complete analysis. The method of preparation was essentially that of Bouquet and Cloez. The first sample was prepared by passing a rapid current of sulphuretted hydrogen through 250 cc. of a solution of dihydrogen-potassium arseniate, saturated in the cold, for about two hours. A little hydrate of potassium was added every now and then. The addition of this reagent seems to facilitate the separation of the salt, but it is not necessary, for the crystals obtained in the preliminary work separated out of the *strongly acid* solution of the potassium arseniate without any addition what-

ever of hydrate of potassium. The mother-liquor and the sulphide of arsenic were poured off and filtered, and the crystals having been brought into a platinum dish, were repeatedly washed with portions of the filtrate from the sulphide of arsenic until all yellow specks had been removed. The washing was continued with very small quantities of water, and ended with 90 per cent. alcohol and with ether. This washing with alcohol and ether rendered the final drying and purification by pressing between folds of filter paper unnecessary. The salt was allowed to remain in a vacuum and over concentrated sulphuric acid for several days, but this was really unnecessary, as I have since found that the salt after washing with alcohol and with ether is, after the ether has evaporated, perfectly dry.

The second sample was prepared in the same way, with the exception that the solution of dihydrogen-potassium arseniate, after the treatment with the gas, was allowed to stand over night in a cool place. The crop of crystals thus obtained was larger than that resulting in the first case. As Bouquet and Cloez, however, have already pointed out, the quantity of sulphoxyarseniate of potassium obtained is always extremely small in comparison with the quantity of arseniate of potassium used. The sulphoxy-salt is somewhat more difficultly soluble in water than the ordinary arseniate, but the difference is not very marked, and therefore the quantity of the sulphoxy-salt which separates is necessarily small.

Analyses.

The salt in each case was oxidised with fuming nitric acid. The moment the acid came in contact with the crystals, a cake of sulphur separated out, which was gradually oxidised to sulphuric acid.

The arsenic in I was determined as arseniate of silver;[1] the oxygen according to Bunsen's method; the potash as the double chloride of platinum and potassium; and the water, directly, by very carefully heating a portion of the sample in a glass tube in a current of dry air—the part of the tube directly in front of the boat containing the substance being plugged with a roll of strongly ignited copper gauze.

The arsenic in II was determined as the pentasulphide, according to my own method;[2] the oxygen was done by difference; and the potash and water exactly as in I.

[1] This Journal **8**, 77. [2] Ibid. **9**, 174.

	Calculated for $H_3KAsO_3.S$.	Found.[1] I.	II.
As	38.27	38.29	38.36
S	16 35	15.60[2]	16.12
O	12.25	12.62	12.10
K_2O	23.98	23.91	23.96
H_2O	9.15	9.59	9.46
	100.00	100.01	100.00

A good deal of care must be taken in determining the water, owing to the fact that in heating the salt, a little arsenious acid is apt to sublime, and in spite of the copper gauze, pass partially into the chloride of calcium tube. I have found that by heating the solution of potassium arseniate saturated in the cold to boiling, removing the source of heat, and then treating the liquid with a rapid current of sulphuretted hydrogen until cold, the sulphoxyarseniate is formed more rapidly and in larger quantities. A considerable amount of sulphide of arsenic and sulphur separates out, but these can be easily removed by washing.

The reactions of a solution of potassium sulphoxyarseniate were compared very carefully with those of the liquid obtained by treating an acidified cold or warm solution of an alkali arseniate with a slow current of sulphuretted hydrogen, but no difference could be observed.

Sulphoxyarsenic acid and its salts can be distinguished from soluble sulphides by the fact that when mineral acids are added to dilute solutions, no sulphuretted hydrogen is evolved. The salts differ from sulpho-salts in that they are not precipitated in dilute solution by mineral acids. They cannot be mistaken for hyposulphites, for their solutions when heated with mineral acids give off no sulphur-dioxide, and their conduct toward silver solution is entirely different. Sulphoxyarsenic acid, it will be remembered, gives with silver solution instantaneously a jet-black precipitate of sulphide of silver, whereas in the case of a hyposulphite, the pre-

[1] Bouquet and Cloez found:

As	38.02
S	16.10
O	12.43
K_2O	23.69
H_2O	9.50
	99.74

For further information, see their memoir in the Annales de Chimie et de Physique, 3 Serie, **13**.

[2] Another determination gave 16.21 per cent. sulphur.

cipitate obtained with this reagent is first white, then yellow, next red, followed by brown, and finally black.

It should also be added that an ammoniacal solution of sulphoxyarsenic acid gives with silver solution a black precipitate of sulphide of silver. This reaction will remind one of pentathionic acid, but pentathionic acid reduces indigo, and sulphoxyarsenic acid does not.

A solution of sulphoxyarseniate of potassium when rendered strongly ammoniacal gives no precipitate with magnesia mixture. This reaction will serve to distinguish sulphoxyarsenic acid from arsenic acid.

Rose's Experiment.

The mystery, then, which for so many years has been connected with the action of sulphuretted hydrogen on arsenic acid, here finds complete solution. The only wonder is that it has not been solved long ago. Rose undoubtedly had the sulphoxyarsenic acid in his hands when he was engaged in his study of the action of sulphuretted hydrogen on arsenic acid. He says distinctly that after treating the solution of arsenic acid for a short time with sulphuretted hydrogen, sulphur separates, which long remains suspended in the liquid. He says he had to let his liquid stand several days, and had to heat it repeatedly in order to collect the finely divided sulphur and render it possible to filter it off and get a clear filtrate. It seems to me hardly possible that after all this standing and heating, a solution which at first contained but a small amount of sulphuretted hydrogen could still retain enough of the gas to give with silver solution a black precipitate of sulphide of silver. And yet Rose, when he added silver solution to the filtrate from the sulphur, did get a black precipitate of sulphide of silver. In the light of the experiments described above, it appears highly probable that the black precipitate of sulphide of silver was occasioned by the presence, in the liquid undergoing examination, of sulphoxyarsenic acid, and not, as was thought, by the presence of free sulphuretted hydrogen.

I have found, indeed, that very dilute solutions of sulphoxyarsenic acid, even when exposed to the air and light, will keep for a long time. A dilute solution of the acid which had stood for over a month, still gave the silver reaction with a considerable degree of sharpness. Before testing with the silver solution, I was of course careful to remove with asbestus all sulphur which had separated.

One will undoubtedly be here reminded of the extreme difficulty so often experienced in precipitating with sulphuretted hydrogen the last trace of arsenic as sulphide from an acidified solution of arsenic acid. The directions usually given for precipitating arsenic with sulphuretted hydrogen from solutions of arsenic acid are, to acidify strongly with hydrochloric acid, heat to boiling, saturate with the gas, and let the liquid so treated stand in a warm place until all smell of sulphuretted hydrogen has disappeared. Now, as my experiments go to show, unless the gas be passed for many hours, the liquid, after standing until all smell of sulphuretted hydrogen has disappeared, will contain large quantities of sulphoxyarsenic acid. If a portion of such a liquid as that here referred to be filtered and tested with sulphuretted hydrogen, a precipitate of trisulphide of arsenic is almost sure to result, and if the rest be allowed to stand, especially in a warm place, the chances are that it will slowly cloud up, sulphur will be deposited, and more arsenious acid will be formed. If a portion be now tested with sulphuretted hydrogen, a heavier precipitate of trisulphide of arsenic will appear.

It will be at once seen how admirably the presence and mode of decomposition of the sulphoxyarsenic acid, as represented in the following equation:

$$2(H_3AsO_3S) = As_2O_3 + 3(H_2O) + 2S,$$

accounts for the sluggish precipitation of the arsenic with sulphuretted hydrogen from an acidified solution of arsenic acid, and how satisfactorily it explains the formation, when the current of gas is slow, of the mixture of pentasulphide, trisulphide, and sulphur.

Recapitulation.

When sulphuretted hydrogen acts upon an *acidified* solution of arsenic acid, the end-products are either: *A.* sulphoxyarsenic acid; *B.* pentasulphide of arsenic; or *C.* a mixture of pentasulphide of arsenic, trisulphide of arsenic, and sulphur.

A. Sulphoxyarsenic acid is the end-product.—This will be the case provided the amount of sulphuretted hydrogen which has acted on the arsenic acid is, in comparison with the amount of arsenic acid in the dilute solution, extremely small (McCay).

$$(1)\ H_3AsO_4 + H_2S = H_3AsO_3S + H_2O.$$

B. Pentasulphide of arsenic is the end-product.—This will be the case provided the solution of arsenic acid be kept saturated with sulphuretted hydrogen. We can here distinguish four cases: *a.* pentasulphide of arsenic is alone formed provided the solution of arsenic acid be kept hot and a rapid stream of sulphuretted hydrogen be passed through it for a long time (Bunsen); *b.* the pentasulphide will be alone formed provided the solution of arsenic acid be brought into a bottle, the bottle almost filled with freshly boiled cold water, the liquid saturated with sulphuretted hydrogen, and the whole, after the bottle has been tightly corked, placed in a bath of boiling water for one hour (McCay); *c.* the pentasulphide will be alone formed provided the cold solution of arsenic acid be treated with a rapid stream of sulphuretted hydrogen for an indefinitely long time (Brauner and Tomiček); and *d.* the pentasulphide will be alone formed provided the cold solution of arsenic acid be brought into a bottle, the bottle almost filled with pure water, the liquid saturated with sulphuretted hydrogen, and the whole, after the bottle has been tightly stoppered, permitted to stand for two weeks (McCay). I offer the following figures as a proof of this last statement:

Solution used, 25 grams of H_2KAsO_4 in 2000 cc. H_2O.

	Taken.	Calculated.	Found.
1.	25 cc. Standard H_2KAsO_4	= 0.2670 gram As_2S_5.	0.2675 gram As_2S_5.
2.	25 cc. Standard H_2KAsO_4	= 0.2670 " "	0.2669 " "
3.	50 cc. Standard H_2KAsO_4	= 0.5340 " "	0.5350 " "

(1) $H_3AsO_4 + H_2S = H_3AsO_3.S + H_2O.$

(2) $2H_3AsO_3.S + 3H_2S = As_2S_5 + 6H_2O.$

C. A mixture of pentasulphide of arsenic, trisulphide of arsenic, and sulphur, is the end-product.—This will be the case provided the warm or cold solution of arsenic acid be not saturated, or saturated but not kept saturated, with sulphuretted hydrogen. Here we have far more sulphuretted hydrogen than in *A*, but not nearly so much as in *B*. The solution may be heated, say to 70° C., and a very slow current of the gas passed into it for a long or short time. Here then would result, owing to the heat, a constant and rapid loss of gas. The liquid as a whole is never saturated; or the solution may be saturated with sulphuretted hydrogen, and then allowed

to stand. A continuous escape of gas would ensue, and the liquid would soon lose its original strength. The rate of loss of gas by volatilisation is greater than the rate of formation of the pentasulphide. The solution, in a word, does not remain saturated. It must always be borne in mind that, to obtain the pentasulphide alone, the solution of arsenic acid must be kept saturated with sulphuretted hydrogen. In both cases then, there being no constant excess of gas, the conditions for the formation, temporary existence, and decomposition of the sulphoxyarsenic acid are favorable. The formation of the mixture may be imagined to take place in the following way: The sulphuretted hydrogen first acts upon the arsenic acid, changing it to sulphoxyarsenic acid. The sulphoxyarsenic acid, moreover, at those points in the liquid where the gas is in excess—at the point where the gas enters and about the surfaces of the ascending bubbles of gas—is changed slowly to *pentasulphide* of arsenic, and precipitated as such. At other points in the liquid, however, where there is a lack of gas—say, perhaps, to mention only one, along the side of the beaker farthest from the end of the delivery tube—the sulphoxyarsenic acid decomposes, in part, into arsenious acid, water, and *sulphur*. The arsenious acid is then acted upon by the sulphuretted hydrogen and precipitated as the *trisulphide*.

I maintain that there is no reduction of arsenic acid, by sulphuretted hydrogen, to arsenious acid. The trisulphide found in the mixture is the result of the splitting up of the sulphoxyarsenic acid into arsenious acid, water, and sulphur, and the precipitation of the former as trisulphide by sulphuretted hydrogen.

(1) $H_3AsO_4 + H_2S = H_3AsO_3.S + H_2O$;
(2) $2H_3AsO_3.S + 3H_2S = As_2S_3 + 6H_2O$;
(3) $2H_3AsO_3.S + 6HCl = As_2Cl_6 + 6H_2O + 2S$;
(4) $As_2Cl_6 + 3H_2S = As_2S_3 + 6HCl$.

Conclusion.

In closing, I call especial attention to the interesting character of sulphoxyarsenic acid, whose ability to exist in the free state has now, I trust, been amply demonstrated. Whether this acid is the same as that corresponding to the several sodium salts prepared by K. Preis, I cannot at present say. Preis mentions but one characteristic reaction, which is, that solutions of the salts, when saturated with hydrochloric acid and boiled, decompose, with separation of

pentasulphide of arsenic. This reaction is not given by sulphoxyarsenic acid or sulphoxyarseniate of potassium prepared as above described. The solutions of this acid are, as I have repeatedly shown, decomposed when boiled with an acid, but into arsenious acid, water, and sulphur. Can it be that Preis's salts are isomorphic mixtures of sodium arseniate and sodium sulpharseniate? The reaction with hydrochloric acid would indicate such a possibility. The point is an important one and worthy of further investigation. I regret to say that I have been unable to consult Preis's original article. My information respecting his work has been obtained from an abstract from the *Chemiké Listy* which appeared in the Repertorium of the *Chemiker Zeitung*, 1888, 23, 73. In regard to this matter I hope to have more to say before long.

JOHN C. GREEN SCHOOL OF SCIENCE,
PRINCETON, N. J., *June* 1, 1888.

ON THE OXIDATION OF BENZENE DERIVATIVES WITH POTASSIUM FERRICYANIDE.[1]

BY W. A. NOYES.

V.

In a previous paper[2] it has been shown that when the three nitro-toluenes are oxidised in exactly the same manner by an alkaline solution of potassiun ferricyanide, the para and ortho compounds are converted into nitro-benzoic acids with much greater ease than the meta compound. In conclusion, the opinion was expressed that in potassium ferricyanide would be found an agent by means of which a methyl group which is ortho to a nitro group in a benzene derivative can be oxidised, while a methyl group which is meta to the same nitro group is left unoxidised. Experiments to test the correctness of this view were commenced

[1] Since the manuscript of this article left my hands, two articles, by St. Niementowski (Ber. d. chem. Ges. **21**, 1534), and by St. Niementowski and Br. Rosanski (*ibid.* **21**, 1992), have been received, which cover, in part, the same ground. They give the melting point of β-nitro-p-toluic acid as 161°, a little lower than found by myself. The barium salt is reported as containing $4H_2O$, but it was precipitated by alcohol, while mine was crystallised from water. Their calcium salt is reported as without water of crystallisation, though for some reason which is not apparent, the salt was dried at 190°. In other respects their results agree essentially with mine.

[2] This Journal **7**, 149.

soon afterwards, but, owing to a variety of causes, the work has been much delayed.

The substance naturally chosen for study was nitro-para-xylene, since it contains one methyl group in the ortho and a second in the para position with reference to the nitro group. The oxidation was at first attempted with a nitro-para-xylene obtained from Kahlbaum. This boiled from 234° to 244° and chiefly from 235°–240°. It gave a mixture of acids from which it was almost impossible to separate any pure substance. It is, perhaps, of some interest to notice, in passing, that one of the products of oxidation seemed to be terephthalic acid. Landolph[1] and Fittica[2] oxidised substances which they supposed to be nitrocymene, with chromic acid, and obtained acids which they called β and γ-nitro-para-toluic acids. These sublimed without melting at a temperature above 300°. Since von Gerichten[3] has shown that the β-nitro-cymene used was not a nitro-cymene at all, and since Widman and Bladin[4] have shown that nitro-cymene cannot be obtained by the method used by Landolph and Fittica, it seems at least probable that the so-called β-nitro-para-toluic acid was in reality terephthalic acid. That the true β-nitro-para-toluic acid has entirely different properties from those of either of the acids obtained by Fittica, will be shown farther on.

For the experiments which were finally successful, nitro-para-xylene was prepared from pure para-xylene by nitrating it with a cooled mixture of nitric acid (sp. gr. 1.40), with a little more than twice its weight of conc. sulphuric acid. The nitration was conducted essentially as described by Nölting and Forel.[5] The nitro-xylene obtained was thoroughly washed with caustic soda, and was distilled two or three times with water vapor. The first and last portions were kept separate from the rest. Lazarus[6] has shown that by distillation with water vapor a hydrocarbon can be almost quantitatively separated from a nitro compound. For small quantities the method is certainly very much better than ordinary fractional distillation. The nitro-xylene obtained in this way, after drying, boiled entirely between 235° and 240°, and fully three fourths of it from 237° to 238° (uncor.). This portion was used for the experiments described below.

[1] Ber. d. chem. Ges. **6**, 937. [2] Ibid. **7**, 1357, and Ann. Chem. (Liebig) **172**. 316.
[3] Ibid. **11**, 1092. [4] Ber. d. chem. Ges. **19**, 584. [5] Ibid. **18**, 2680. [6] Ibid. **18**, 578.

Oxidation of Nitro-para-xylene.

The oxidation was conducted essentially as described in former papers. From 4 to 7 cc. of the nitro-xylene were boiled for three or four hours with 100 grams of potassium ferricyanide, 40 grams of caustic potash, and 400 cc. of water. The oxidation was conducted on a sand-bath in a flask closed with a cork in which was fitted a piece of combustion tubing about one meter long, to act as a condenser. At the end of three or four hours the nitro-xylene which remained unoxidised was distilled off with water vapor. It was then used for a second oxidation. The solution remaining in the flask was filtered and allowed to cool till the potassium ferrocyanide had crystallised as far as possible. The solution was then acidified with hydrochloric acid and extracted with ether. The acids were then converted into the barium salts, but the attempt to separate pure salts from the mixture was not successful.

The separation and identification of the products of oxidation were finally effected by a different method of treating the solution from which the potassium ferrocyanide had been crystallised. To this was added enough hydrochloric acid to render the solution only very slightly acid. This seems to set free chiefly the monobasic acid, and on extracting with ether, a product was obtained which could be easily purified by crystallising two or three times from hot water.

The purified substance proved to be β-nitro-para-toluic acid. It crystallised in fine needles which retain a slight yellow color. It melts at 164°–165° (cor.) It is easily soluble in hot water, more difficultly soluble in cold water, easily soluble in alcohol and ether.

The analyses were as follows:

I. 0.1096 gram of the acid gave 0.00812 gram N.

II. 0.2163 gram of the acid gave 0.4192 gram CO_2 and 0.0754 gram H_2O.

	Calculated for $C_6H_3\begin{cases}CO_2H\\NO_2\\CH_3\end{cases}$.	Found. I.	Found. II.
N	7.73	7.50	...
C	53.04	...	52.86
H	3.87	...	3.87

The copper salt of the acid was also prepared by adding a hot solution of the calcium salt to a solution of copper chloride. The salt separated in microscopic crystals having a bright green color and almost insoluble in hot or cold water. As will be seen later,

the normal copper salt of the isomeric nitro-para-toluic acid consists of blue needles containing four molecules of water. The analysis of the salt was as follows:

0.0560 gram of the salt lost 0.0025 gram H_2O at 170° and gave 0.0101 gram CuO.

$$\left(C_6H_3\begin{cases}CO_2\\NO_2\\CH_3\end{cases}\right)_2 Cu + H_2O.$$

			Found.
$(C_8H_6O_4)_2$	360.	...	...
Cu	63.3	14.34	14.40
H_2O	18.	4.08	4.46
	441.3		

The method of preparing β-nitro-para-toluic acid which has been described is tedious and the yield is small. In view of the work of Fittica which has been referred to, it seemed of interest to prepare the acid in sufficient quantity for a more careful study of its properties. Sandmeyer[1] has given us a method by which the preparation of the acid is comparatively easy.

The substance necessary for the synthesis of the acid is nitro-para-toluidine, $C_6H_3\begin{cases}CH_3\ 1.\\NO_2\ 3.\\NH_2\ 4.\end{cases}$, (melting point 116°). This was prepared by the method of Gattermann,[2] slightly modified. Para-toluidine was boiled for four or five hours with about twice its weight of glacial acetic acid. The solution was poured into water, and the precipitated acettoluide was washed and dried. 32 grams of this para-acettoluide were added quite rapidly to a mixture of 118 cc. of nitric acid (sp. gr. 1.40), with 47 cc. of sulphuric acid (sp. gr. 1.84). The mixture was vigorously stirred and placed in cold water, so that the temperature varied between 30° and 40° during the addition of the acettoluide. The solution was allowed to stand for fifteen minutes, and was then poured carefully in about 700 cc. of water. The precipitated nitro-acettoluide was filtered with a D. O. Witt filtering plate, washed, and pressed together on the plate to remove as much as possible of the water. It then weighed, in moist condition, 82 grams, and was at once put into a flask with 75 cc. of strong alcohol. The mixture was heated on the water-bath till solution was nearly complete, and then 16 grams of caustic potash dissolved in 20 cc. of water were carefully added. The heating was continued for 15 to 20 minutes. The solution

[1] Ber. d. chem. Ges. **18**, 1492. [2] Ibid. **18**, 1482.

was then cooled rapidly, and the nitro-toluidine which separated was filtered off and washed with alcohol of 30 per cent. The nitro-toluidine obtained in this way seemed to be perfectly pure and weighed 27.5 grams. By the method described, para-toluidine yields somewhat more than its own weight of nitro-toluidine, and the preparation requires but little time.

Nitrile of β-Nitro-para-toluic Acid.

The conversion of the nitro-toluidine into the cyanide was conducted as described by Sandmeyer.[1] A somewhat larger amount of potassium cyanide was used, however, in order to prevent the separation of cuprous cyanide at the end of the reaction. The solution of cuprous cyanide was prepared by adding carefully a solution of 33 grams of potassium cyanide to a hot solution of 28 grams of crystallised copper sulphate in about 150 cc. of water. 15.2 grams of the finely powdered nitro-toluidine were put in a flask with 500 cc. of cold water. 8.6 grams of potassium nitrite and 26 cc. of hydrochloric acid (sp. gr. 1.128) were added, the flask was corked, and the mixture shaken vigorously for ten minutes. The diazo compound which was formed remained dissolved, and the solution was filtered quickly from a small portion of the nitro-toluidine which remained unconverted. The latter, if washed at once with water, is pure enough for use in a second operation. The solution containing the diazo compound has a light permanganate red color, caused apparently by a slight decomposition. The solution containing the cuprous cyanide was placed over a vigorous flame and kept at a temperature of about 70°, while the diazo solution was added as rapidly as it could be without lowering the temperature too much. At the temperature mentioned, the cyanide formed separates as a yellowish brown solid, while, if the temperature is slightly higher, it separates as a dark colored oil which is apparently less pure. When the reaction was complete the solution was cooled rapidly and the cyanide was filtered off at once. The yield is very good, and the product is pure enough for conversion into the acid.

For analysis the cyanide was crystallised once or twice from hot water. On cooling the hot solution it separates in fine needles which when pure are almost white, but which usually have a light yellow color. It is moderately soluble in ether, and separates, on

[1] Loc. cit.

spontaneous evaporation of the solution, in short thick prisms. It is easily soluble in alcohol. It melts at 100°. 0.1234 gram of the substance gave 0.0217 gram of N, which corresponds to 17.59 per cent. Theory requires 17.29 per cent.

β-Nitro-para-toluic Acid.

Sandmeyer saponified the cyanides of the nitro compounds with which he worked by boiling with an aqueous solution of caustic soda. The same method applied to this cyanide caused the formation of a mixture of substances from which it was almost impossible to separate anything in pure condition. Good results were obtained, however, by heating in sealed tubes with concentrated hydrochloric acid. From ten to fifteen parts of the acid were used to one of the cyanide, and the heating was continued from one to two hours at a temperature of 150° to 160°. On cooling, the portion which had passed into solution separated in long and rather thick needles which were almost perfectly white. The acid was purified by solution in dilute ammonia, filtering, precipitating with hydrochloric acid, and recrystallising from hot water. The pure acid melted at 164°–165° (cor.), and had the same properties as those of the acid obtained by the oxidation of nitro-xylene with potassium ferricyanide.

Barium β-Nitro-para-toluate, $\left(C_6H_3\begin{cases}CO_2\\NO_2\\CH_3\end{cases}\right)_2Ba + 5H_2O$.—The barium salt was prepared in the usual way. It is easily soluble in water, and has a tendency to form supersaturated solutions. On cooling a hot, moderately concentrated solution, it separates in crystals radiating from centers and forming half-balls on the bottom of the beaker or top of the liquid. If very concentrated, the solution is converted into a solid mass of crystals. The salt, as it at first separates, seems to contain *nine and one-half* molecules of water. Two analyses of a salt air-dried for a short time gave, respectively, 25.53 and 25.99 per cent. of water. Theory requires for 9½ molecules 25.60 per cent. A salt by a new crystallisation, and which was dried by pressing between filter paper, gave but 21.33 per cent. of water, however, and when air-dry for two or three days in a rather warm room, the salt contains but *five* molecules of water. The salt loses its water slowly but almost completely over sulphuric acid. The other determinations of water were as follows:

I. 0.1607 gram of the salt air-dried for two days lost 0.0247 gram H_2O at 135°.

II. 0.4103 gram of the salt air-dried for 28 hours in a warm room lost 0.0647 gram H_2O at 135°.

III. 0.1722 gram of a salt which was allowed to stand over sulphuric acid with very frequent weighings till a point was reached when it ceased to lose weight rapidly, lost 0.0272 gram H_2O at 135°.

	Calculated for $\left(C_6H_3\begin{matrix}CO_2\\-NO_2\\CH_3\end{matrix}\right)_2Ba+5H_2O$.	Found.		
		I.	II.	III.
$5H_2O$	15.33	15.37	15.77	15.80

The determinations of barium were as follows:

I. 0.2054 gram of the dry salt gave 0.0961 gram $BaSO_4$.

II. 0.1788 gram of the dry salt gave 0.0832 gram $BaSO_4$.

III. 0.1896 gram of the dry salt gave 0.0882 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{matrix}CO_2\\-NO_2\\CH_3\end{matrix}\right)_2Ba$.		Found.		
			I.	II.	III.
$(C_8H_4NO_4)_2$	3.60	...	...	...	...
Ba	1.37	27.56	27.51	27.37	27.36

Calcium β-Nitro-para-toluate, $\left(C_6H_3\begin{matrix}CO_2\\-NO_2\\CH_3\end{matrix}\right)_2Ca+2H_2O$.—The calcium salt is much more difficultly soluble than the barium salt. It seems to be about equally soluble in hot and cold water. By evaporating on the water-bath, the salt is deposited from the hot solution in needles. If these are filtered off, the filtrate deposits nothing on cooling. The same salt separates by the spontaneous evaporation of the cold solution, forming a network of needles which creep up and cover the walls of the beaker. This property is very characteristic of the salt. In determining the water of crystallisation it was found that the salt melted partially at 170°. Heated rapidly in a capillary tube it forms a glossy mass at 180°–185°, but does not become entirely liquid.

The analyses were as follows:

I. 0.1786 gram of the salt deposited by the hot solution lost 0.0148 gram H_2O at 170°, and gave 4.0550 gram $CaSO_4$.

II. 0.2173 gram of the salt deposited by the cold solution lost 0.0175 gram H_2O at 170°, and gave 0.0672 gram $CaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}CO_2\\NO_2\\CH_3\end{cases}\right)_2Ca + 2H_2O$.		Found. I.	Found. II.
$(C_8H_6NO_4)_2$	360	...	...	...
Ca	40	9.17	9.06	9.10
$2H_2O$	36	8.26	8.29	8.05
	436			

Copper β-Nitro-para-toluate, $\left(C_6H_3\begin{cases}CO_2\\NO_2\\CH_3\end{cases}\right)_2Cu + H_2O$.—This was prepared by adding a solution of the calcium salt to a solution of copper chloride. It separates at first as an amorphous precipitate, but on warming it is quickly converted into microscopic crystals of a bright green color. This salt is the most characteristic of any of those prepared. It is especially suited to distinguish the acid from the well known α-nitro-para-toluic acid.

I. 0.1051 gram of the salt lost 0.0045 gram H_2O at 160°–170° and gave 0.0188 gram CuO.

II. 0.1619 gram of the salt lost 0.0070 gram H_2O at 168° and gave 0.0290 gram CuO.

	Calculated for $\left(C_6H_3\begin{cases}CO_2\\NO_2\\CH_3\end{cases}\right)_2Cu + H_2O$.		Found. I.	Found. II.
$(C_8H_6NO_4)_2$	360	...	...	...
Cu	63.3	14.34	14.34	14.36
H_2O	18	4.08	4.28	4.33
	441.3			

β-Amido-para-toluic Acid.—This was prepared by reducing the acid with tin and hydrochloric acid. After diluting, precipitating the tin with hydrogen sulphide, and evaporating to a small volume, the chloride of the new acid separated in fine needles, on cooling the strongly acid solution. These were washed with hydrochloric acid of sp. gr. 1.12, in which they were difficultly soluble. After drying, the free acid was obtained by warming the chloride with somewhat less than the calculated amount of very dilute ammonia, cooling and filtering.

As thus obtained, the acid is white and apparently amorphous. It may be obtained in very fine leaflets or plates by crystallising from hot water, but these usually have a brownish color. The acid is difficultly soluble in cold and hot water, easily soluble in

alcohol. Its aqueous solution shows a blue-violet fluorescence, which disappears on adding a strong acid, but returns on adding ammonia. The same fluorescence is shown by the salts. The acid melts at 177°–178° (cor.), and at the same time decomposes with the evolution of a gas. The analyses of the acid were as follows:

I. 0.1312 gram of the acid gave 0.01226 gram N.
II. 0.1335 gram of the acid gave 0.01236 gram N.

	Calculated for $C_6H_3\begin{cases}CO_2H\\NH_2\\CH_3\end{cases}$.	Found. I.	II.
N	9.27	9.34	9.26

Barium β-Amido-para-toluate, $\left(C_6H_3\begin{cases}CO_2\\NH_2\\CH_3\end{cases}\right)_2 Ba + 4H_2O$. — This was prepared as usual by boiling the acid with barium carbonate. It separates, on cooling a hot solution, in brown leaflets or scales which are very difficultly soluble both in hot and cold water. It was not found possible to determine the water of crystallisation directly, as the salt loses only three or four per cent. of water at temperatures below that at which it begins to decompose. The determinations of barium were as follows:

I. 0.1935 gram of the salt gave 0.0885 gram $BaSO_4$.
II. 0.2093 gram of the salt gave 0.0969 gram $BaSO_4$.

	Calculated for $\left(C_6H_3\begin{cases}CO_2\\NH_2\\CH_3\end{cases}\right)_2 Ba + 4H_2O$.		Found. I.	II.
$(C_8H_8NO_2)_2$	300	...	...	...
Ba	137	26.92	26.90	27.23
$4H_2O$	72	14.14	...	...
	509			

Calcium β-Amido-para-toluate, $\left(C_6H_3\begin{cases}CO_2\\NH_2\\CH_3\end{cases}\right)_2 Ca + 2H_2O$. — The attempt to prepare the calcium salt in the usual way, by boiling the acid with calcium carbonate, gave a solution which was acid in reaction. Accordingly the solution was boiled with a slight excess of thin milk of lime, and the excess of lime was precipitated with carbon dioxide. The salt separates in scales which have a slight brown color. The salt loses most of its water at 135°, but there is a slight additional loss at 200°.

The analyses were as follows:

I. 0.1646 gram of the salt lost 0.0157 gram H_2O at 200° and gave 0.0591 gram $CaSO_4$.

II. 0.2034 gram of the salt lost 0.0191 gram H_2O at 200° and gave 0.0729 gram $CaSO_4$.

	Calculated for $\left(C_6H_3\begin{smallmatrix}CO_2\\NH_2\\CH_3\end{smallmatrix}\right)_2 Ca + 2H_2O$.		Found. I.	Found. II.
$(C_8H_8NO_2)_2$	300	...	...	...
Ca	40	10.64	10.56	10.54
$2H_2O$	36	9.57	9.54	9.39
	376			

Copper β-Amido-para-toluate, $\left(C_6H_3\begin{smallmatrix}CO_2\\NH_2\\CH_3\end{smallmatrix}\right)_2 Cu$.—This is obtained as an amorphous, light green precipitate when a solution of copper chloride is added to a solution of the calcium salt. It is almost insoluble in hot or cold water. When air-dry the salt still retains a small amount of water, which it loses at 135°.

I. 0.1037 of the salt dry at 135° gave 0.0223 gram CuO.

II. 0.1061 gram of the salt dry at 135° gave 0.0231 gram CuO.

	Calculated for $\left(C_6H_3\begin{smallmatrix}CO_2\\NH_2\\CH_3\end{smallmatrix}\right)_2 Cu$.		Found. I.	Found. II.
$(C_8H_8NO_2)_2$	300	...	...	...
Cu	63.3	17.42	17.15	17.39
	363.3			

Constitution of β-Amido-para-toluic Acid.

There could be scarcely a question as to the constitution of the nitro and amido-toluic acids which have been described. It was of some interest, however, in view of the work of Fittica, which has been referred to, to furnish a direct proof of the structure by converting the amido acid into a known oxy-toluic acid. For this purpose, about 40 milligrams of the acid were dissolved by shaking with dilute sulphuric acid and a little more than the calculated amount of potassium nitrite. On boiling the solution and cooling, the oxy-acid separated in needles. After boiling with a little bone-black and crystallising from hot water, these were nearly white and melted at 177° (cor.). The acid also gives a violet color with ferric

chloride. These properties are sufficient to characterise it as β-oxy-para-toluic acid, $C_6H_3\begin{cases}CO_2H\ 1.\\OH\ 2.\\CH_3\ 4.\end{cases}$, and the nitro and amido acids must have a similar constitution. It seems almost certain, therefore, that the true β-nitro-para-toluic acid has been described here for the first time, and that the acids prepared by Landolph and Fittica were not nitro-toluic acids.

Nitrile of α-Nitro-para-toluic Acid.

The copper salt of α-nitro-para-toluic acid seems never to have been prepared. A comparison of the salt with that of the β-acid seemed of interest. The acid itself was prepared from nitro-para-toluidine, $C_6H_3\begin{cases}CH_3\ 1.\\NO_2\ 2.\\NH_2\ 4.\end{cases}$ (melts at 78°), by the same method which has been described for the isomeric acid. The cyanide obtained separates at first as a coffee-brown precipitate. It crystallises from a hot aqueous solution in fine white needles which melt at 107°. A determination of nitrogen in the substance gave 17.44 per cent. of N. Theory requires 17.29 per cent. The nitrile was converted into the acid by heating with concentrated hydrochloric acid in sealed tubes, and the calcium salt was prepared in the usual way.

Copper α-Nitro-para-toluate, $\left(C_6H_3\begin{cases}CO_2\\NO_2\\CH_3\end{cases}\right)_2 Cu + 4H_2O$.—When a solution of the calcium salt is added to a hot solution of copper chloride, a light blue amorphous precipitate is obtained which, after washing with hot water, consists of a basic salt of somewhat varying composition. The salt may be dried at 135° without change of color. If it is then heated to 200° it turns green and loses about two per cent. in weight. In two cases the salts gave amounts of water and copper which agree fairly well with the formula $Cu_3\left(C_6H_3\begin{cases}CO_2\\NO_2\\CH_3\end{cases}\right)_4(OH)_2 + H_2O$. A third salt gave a larger per cent. of copper. A fourth gave 42.72 per cent. of carbon, 3.11 per cent. of hydrogen, and 17.01 per cent. of copper. A salt of the formula $Cu_3\left(C_6H_3\begin{cases}CO_2\\NO_2\\CH_3\end{cases}\right)_5 OH + H_2O$ requires 42.67 per cent. carbon, 2.93 per cent. hydrogen, and 16.88 per cent. copper.

The filtrate from the basic salt deposits the normal salt, on

cooling, in the form of bright blue needles mixed with white crystals of the acid. The latter can be easily removed by means of ether. The same salt may be obtained more easily by dissolving 0.4 gram of the calcium salt in 100 cc. of hot water, with the addition of 0.01 gram of hydrochloric acid, and adding 0.2 gram of copper chloride dissolved in 100 cc. of hot water. On filtering and cooling, the salt is deposited as before, in the form of beautiful blue needles.

The analyses were as follows:

I. 0.0991 gram of the salt lost 0.0139 gram H_2O at 135° and gave 0.0159 gram CuO.

II. 0.1591 gram of the salt lost 0.0230 gram H_2O at 135° and gave 0.0253 gram CuO.

	Calculated for $\left(C_6H_3\begin{smallmatrix}CO_2\\NO_2\\CH_3\end{smallmatrix}\right)_2Cu+4H_2O$.		Found. I.	Found. II.
$(C_8H_6NO_4)_2$	360.	...	...	...
Cu	63.3	12.78	12.82	12.70
$4H_2O$	72.	14.54	14.03	14.46
	495.3			

Formation of Nitro-terephthalic Acid.

After removing most of the β-nitro-para-toluic acid from the slightly acidified solution referred to in the early part of this paper, more acid was added, and the solution was extracted again with ether. On recrystallising from hot water the acids obtained, two substances were separated. One of these crystallised in needles aggregated to balls. These melted at 266°–268°, and were evidently nitro-terephthalic acid, which should melt at 270°.[1] The analysis gave 6.75 per cent. of N. Theory requires 6.64 per cent.

The other substance separated in well formed plates. These lose water on heating, and melt at the same temperature as the needles. The analyses of the plates showed that their composition was that of nitro-terephthalic acid, with the addition of two molecules of water. An attempt was made to obtain the same substance by crystallising ordinary nitro-terephthalic acid under various conditions, and with the addition of fragments of the plates; also by oxidising nitro-para-xylene with a strongly alkaline solution of potassium permanganate, and by oxidising β-nitro-para-

[1] Burkhardt, Ber. d. chem. Ges. **10**, 145.

toluic acid with potassium ferricyanide. All of these attempts were unsuccessful, and the only method by which the plates could be obtained was by oxidising the nitro-para-xylene with potassium ferricyanide. They were obtained repeatedly in that way.

These results seem to indicate that the water which the substance loses on heating is not water of crystallisation, but water of constitution. If that is true, the probable formula of the substance is $C_6H_3(NO_2)\begin{cases}C(OH)_3\\C(OH)_3\end{cases}$. The temporary existence of such a substance as the result of oxidation is entirely in accordance with the views ordinarily held with regard to the oxidation of hydrocarbon residues. The more permanent existence of the substance in the present case seems to be analogous to the formation of ortho-sulphamine acids instead of sulphinides, which has been described in previous papers.[1] *In both cases potassium ferricyanide seems to show itself an oxidising agent which resists the formation of anhydro compounds.* Fahlberg and List[2] have recently expressed the opinion that the first product of the oxidation of a sulphamide is a sulphinide, and that the sulphamine acid results from the action of free alkali on the sulphinide. If that method of action held in the present case, the substance which I have described should have been obtained by the oxidation of nitro-para-xylene with the strongly alkaline solution of potassium permanganate, or by oxidising nitro-para-toluic acid with potassium ferricyanide. Neither method gave it. A more natural explanation in the present case seems to be that the hydrogen of the hydroxyl groups formed by oxidation is at once replaced by potassium, and that the presence of the metal resists the formation of an anhydride in the same manner that it does in carbonates. It seems probable that a similar explanation holds in the case of the sulphamides. It has been shown[3] repeatedly that the hydrogen of the sulphamide group can be replaced by metals, and in the strongly alkaline solution it is probable that both hydrogen atoms are so replaced. The presence of the metal might then act to prevent the formation of the anhydride much as in the case described in the present paper. This view seems to me more natural than the one proposed by Fahlberg. It is entirely consistent with the conversion of sulph-

[1] This Journal **8**, 179, and **9**, 94. [2] Ber. d. chem. Ges. **21**, 244.
[3] Wolkow, Ber. d. chem. Ges. **3**, 424. This Journal **8**, 181.

inides into sulphamine acids by the action of alkalies, and that is the chief fact brought forward in support of his view.

I am unable to give any explanation as to why the alkaline solution of potassium ferricyanide should act differently from an alkaline solution of potassium permanganate (really containing potassium manganate) as it has been shown to do in this paper.

The analyses of the plates were as follows:

I. 0.1174 gram of the substance gave 0.00677 gram N.

II. 0.0755 gram of the substance lost 0.0110 gram H_2O at 135°.

	Calculated for $C_6H_3\begin{cases}C(OH)_2\\NO_2\\C(OH)_2\end{cases}$.	Found. I.	II.
N	5.67	5.77	...
$2H_2O$	14.57	...	14.19

Oxidation of Mono-nitro-meta-xylene.

Nitro-meta-xylene (from Kahlbaum) was oxidised in the same manner as the nitro-para-xylene. The acids obtained were converted into the barium salts, and from these the salt of a bibasic acid was easily separated in pure condition. A small amount of a more easily soluble salt was also formed, but attempts to purify it were not successful. Its presence indicates the formation of a small amount of a monobasic acid. The oxidation of nitro-meta-xylene takes place much more easily than that of nitro-para-xylene. The oxidation of nitro-meta-xylene can be effected still more easily with potassium permanganate and the same acid is formed.

β-Nitro-isophthalic Acid.

The acid was separated from the purified barium salt by warming it with a slight excess of very dilute hydrochloric acid till it passed into solution. On cooling the solution the acid separated in small granular crystals having a slight yellow color. Under a good glass the crystals were seen to consist of very small, short needles.

The analysis was as follows:

0.1048 gram of the acid gave 0.00686 gram N.

	Calculated for $C_6H_3\begin{cases}CO_2H\\CO_2H.\\NO_2\end{cases}$	Found.
N	6.64	6.54

The acid obtained by oxidation with potassium ferricyanide

melts at 257°–258° (cor.). That obtained by oxidation with potassium permanganate melts at 258°–259°. The acid is easily soluble in hot water, more difficultly soluble in cold water. It seems to be identical with the β-nitro-isophthalic acid which is formed in small amount when isophthalic acid is treated with fuming nitric acid,[1] and which melts at 260°. Beyer does not seem to have established the constitution of his acid, probably because he obtained it in too small amount. Since Harmsen[2] has shown that the asymmetric nitro-meta-xylene is formed when meta-xylene is nitrated, the constitution of the acid must be represented by the formula $C_6H_3\begin{cases}CO_2H & 1.\\ CO_2H & 3.\\ NO_2 & 4.\end{cases}$ That this is actually the structure of the acid was established by reducing the acid with tin and hydrochloric acid, and by converting the amido acid obtained into the corresponding oxy acid by Griess' reaction. The asymmetric oxy-isophthalic acid[3] was obtained. It melted with decomposition at 300°–303° (uncor.), and gave an onion-red color with ferric chloride.

Barium β-Nitro-isophthalate, $C_6H_3\begin{cases}CO_2\\ CO_2\\ NO_2\end{cases}Ba + 1\frac{1}{2}H_2O$.—When the acids which have been referred to are converted into the barium salts, these pass into solution readily and appear to be quite easily soluble. If the solution is evaporated and the salt deposited, however, a considerable amount of water and prolonged heating are necessary to bring it again into solution. The salt is deposited from the hot solution, during evaporation, in small needles or prisms of a light yellow color. The salt loses its water very rapidly and almost entirely on standing over calcium chloride. The salt for the third analysis was from the acid obtained by oxidation with potassium permanganate. The other salts were from the oxidation with potassium ferricyanide.

I. 0.2541 gram of the salt lost 0.0174 gram H_2O at 132° and gave 0.1593 gram $BaSO_4$.

II. 0.2967 gram of the salt lost 0.0205 gram H_2O at 132° and gave 0.1855 gram $BaSO_4$.

III. 0.3242 gram of the salt lost 0.0206 gram H_2O and gave 0.2037 gram $BaSO_4$.

[1] Beyer, J. prakt. Chem. (2) **22**, 352. [2] Ber. d. chem. Ges. **13**, 1558.
[3] Remsen and Iles, this Journal **1**, 132.

	Calculated for $C_6H_3{<}^{2(CO_2)}_{CO_2}{>}Ba + 1\frac{1}{2}H_2O$.		I.	Found. II.	III.
$C_8H_3NO_8$	209	...	...	...	...
Ba	137	36.73	36.86	36.76	36.95
$1\frac{1}{2}H_2O$	27	7.24	6.85	6.91	6.35
	373				

ROSE POLYTECHNIC INSTITUTE, *May* 5, 1888.

ANALYSIS OF SOME SOUTHERN FRUITS WITH REFERENCE TO THEIR FOOD VALUES.

BY CHARLES L. PARSONS.

König, in his well known work, "Nahrungs- und Genussmittel," gives a summary of all published analyses of fruits,[1] their nutritive ratio and food units. This summary contains the analyses of a large number of fruits, but singularly enough, but one analysis of oranges is given, and that was made previously to the investigation by Buignet, in which the existence of cane sugar in acid fruits was conclusively proved.[2]

Of late years oranges have become so important both as a food and a luxury, and have become so great a source of wealth to some of our Southern States, especially Florida, that I decided to make food analyses of the prominent varieties grown in that State. I have also made analyses of pomegranates and persimmons, which, although seldom seen in the Northern markets, still form no inconsiderable part of the fruits of the South.

For my purpose I obtained direct from a friend in Oviedo, Florida, a box containing eight different varieties of oranges fresh from the grove. The oranges were carefully labeled, and each wrapped in tissue paper. The pomegranates and persimmons were obtained from Hawkinsville, Georgia. I commenced work on the fruits as soon as they arrived. For the analyses a number of oranges were taken of each variety; total acids and water determined in an average sample of the fresh fruit, and the remainder of the pulp dried at about 95° C. Pomegranates and persimmons were treated in the same way, with the exception that the pulp of the persimmons was separated from the seed by means of a large-meshed sieve, previous to drying.

In the following tables I have given a comparison of the dry substance of the fruits analysed, with the dry substance of bread, cocoanut, and banana, giving their nutritive ratio and number of food units. I selected the Navel as a type of the Florida oranges

[1] König, Nahrungs- und Genussmittel, 2d edition, Bd. II, S. 491-497.
[2] Ann. de Chim. et de Phys. [3d series], **61**, 233.

in this comparison, and the Guy Pope, a Messina orange, sold last season in large quantities from New York City, as a type of the Mediterranean orange, of which more than two million dollars' worth are annually imported.

The following results are averages of my analyses:

	H_2O.	Crude Protein	Free Acids.	Glucose Sugar	Cane Sugar.	Ether Ext.	Crude Fibre.	Ash.	Albuminoid Nitrogen.	Nitrogen Free Extract.
Sweet Pomegranates,	78.27	1.33	.368	11.61	1.04	1.24	2.63	.761	.177	15.77
Sour Pomegranates,	75.41	1.60	1.85	10.40	.26	2.05	2.83	.544	.203	17.57
Persimmons,	66.12	.827	.000	13.54	1.03	.701	1.78	.861		29.711
Fla. Orange, Bitter Sweet	86.86	.815	.417	5.71	.84	.243				
Fla. Orange, Tangerine,	83.56	.792	.477	6.00	3.41	.256				
Fla. Orange, Mandarin,	79.95	.834	.855	4.77	8.07	.146				
Fla. Orange, Bloods	85.57	.700	.670	5.70	3.94	.100				
" Navels	83.70	1.12	.662	6.03	4.68	.234				
" Russets	83.18	.905	.817	7.29	4.51					
Fla. Orange, Common Florida,	86.58	.862	.756	4.60	4.38	.076				
Fla. Orange, Fla. Sour,	86.76	1.03	2.55	3.86	.97	.125				
Messina Orange, Guy Pope,	86.22	.980	1.18	5.95	1.82	.166				

	Ntg = Protein.	Fat.	Nitrogen—free Extract = N.Ntg.	Nutritive Ratio Ntg. N.Ntg + (fat × 2.5) :: 1 :	Food Units in 1 kilo Ntg.: fat: N.Ntg :: 5 : 3 : 2.
Bread,	10.94	87.97	.71	8.7	1446.2
Sweet Pomegranates,	6.12	72.52	5.70	13.5	1202.2
Sour Pomegranates,	6.50	71.44	8 34	13.4	1289.6
Persimmons,	2.44	90.63	2.07	38.6	1090.4
Banana,	6.94	85.72	2.33	12.9	1274.1
Solid portion Cocoanut,	10.31	15.10	67.33	12.9	2686.4
Mandarin Orange,	4.15	85.88	.73	21.	1088.2
Navel Orange,	6.87	80.85	1.44	12.1	1195.2
Guy Pope Orange,	5.78	71.11	1.22	12.7	1036.7

Nutritive Ratio = Ntg : N.Ntg + (fat × 1.75) :: 1 : —

To any one who is acquainted with the flavor and general edibility of the different varieties of Florida oranges, it will be apparent that these analyses indicate that the best varieties contain the highest percentages of cane sugar, and that if the analysed varieties were to be placed in the order of their superior flavor, and in the order of their contents of cane sugar, the two series would be very nearly identical.

ANNOUNCEMENT.

From January, 1889, when Vol. XI will begin, THE AMERICAN CHEMICAL JOURNAL will appear in eight numbers a year, instead of six as heretofore. As far as may be practicable, one number of about 72 pages will be issued each month of the year, excepting July, August, September, and October. For some time past the supply of articles submitted for publication has been so great as to require the entire space of the Journal, and the editor has found it impossible to continue the reviews, reports and abstracts which formed a somewhat prominent feature of the earlier volumes. It is proposed now to restore this feature, and a strong effort will be made to secure such reviews and reports as will give a fair idea of the progress of chemistry in its various branches. In consequence of the increase of size, the price will be raised from $3 to $4 a volume.

Hereafter all communications in regard to subscriptions should be addressed to the *Publication Agency of the Johns Hopkins University, Baltimore, Md.*; and editorial communications to the Editor, IRA REMSEN, *P. O. Drawer* 2, *Baltimore, Md.*

NOVEMBER, 1888.